

THE CORROSION AND PROTECTION
OF METALS.



THE CORROSION AND PROTECTION OF METALS,

WITH SPECIAL REFERENCE TO THE
PRESERVATION OF ENGINEERING STRUCTURES.

BY

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PREFACE.

THE subject of the corrosion and protection of metals is of such extreme importance that no engineer can afford to neglect it, and yet the literature of the subject is extremely scanty. This arises, no doubt, from the difficulties in the way of making anything like an exhaustive research on the subject, and also from the indifference of the users of metals to their protection.

These notes have been written to supply to some extent the need for information. They give as far as is possible the present condition of our knowledge on the subject. Small as the book is, its preparation has involved no small amount of labour, and a very large number of experiments, some of them extending over a year or more, have been made. The author is, of course, quite conscious that on such a subject practical experience is of more value than mere laboratory experiments, yet the latter are the only possible means of elucidating obscure points.

These notes do not claim to be complete, but rather to represent a preliminary study of the subject, and the author will esteem it a favour if any who come across cases of corrosion in any way out of the common, or

who have experiences of value, will communicate with him, that a second edition, should it be called for, may be extended and improved. That the opinions expressed will be unanimously accepted the author does not hope. Should others have come to different conclusions, he will be very glad to hear and consider the evidence which they can adduce to support their views, since his object is to reach the truth on the subjects under discussion, and to do something towards the better protection of metal work under the various conditions to which it may be exposed.

The author has to thank his assistant, Mr. Claude A. Meiklejohn, for assistance in reading the proofs and in the preparation of the index.

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CHAPTER I.

RUSTING OF METALS.

THE question of the cause and prevention of the corrosion of metals is of such vital importance to the engineer, that no excuse is necessary for bringing it once more under notice, even though there may be nothing new of very great importance that can be said. Indeed, not only is the question of great, but it is of growing importance. Every year the quantity of metal, especially iron and steel, used for structural purposes is increasing, and much of it is being used under such conditions, and with so little care as to its protection, that it seems to promise disaster in the future, and the work which one sees going on day by day seems to indicate that even yet engineers and architects are not sufficiently alive to the dangers of corrosion.

Most people are apt to consider metals as among the most durable of substances, if not as almost indestructible. The engineer who is accustomed to deal with metals does not, of course, labour under this delusion; but he is apt, nevertheless, to under-estimate the importance of corrosion, the rapidity with which it may act, and at the same time the ease—provided due care be given—with which it can be prevented under ordinary circumstances, and the extent to which the durability of structures can thus be increased.

Compared with such materials as stone or pottery, metals used in construction cannot be regarded as being durable materials. There are no very ancient metal structures in this country, or in any other where the climatic conditions are at all similar. Many structures, in metal, which are quite recent show marked signs of decay, and not a few erected at great cost will probably ere long have to be renewed.

It is intended here to discuss briefly the corrosion of the metals in common use under the conditions in which they are most generally used, and the means that have been found most efficient for protecting them.

Only a few metals are sufficiently used under conditions where decay can take place to render such a study of practical interest, and to such metals attention will be restricted. These are: iron and steel in their various forms, such as cast iron, malleable iron, structural steel, copper, and the alloys of copper, with other metals, such as brass and bronze, and, to a less extent, lead, zinc, and aluminium.

The conditions under which the metals will be used vary considerably, but in general they may be divided into three groups, according to the nature of the corrosive agents to which they are exposed:—

- (1) Air and moisture;
- (2) Corrosive gases;
- (3) Corrosive solutions;

some metals being used so as to be exposed to one set of conditions, and others to quite another.

AIR AND MOISTURE.

Structures of iron and steel are mainly exposed to the action of air and moisture, and these, as will be seen, have an almost unlimited power of destruction. Indeed, it is hardly too much to say that, given time, there is nothing that will withstand their united action, which in the end must produce destruction. The rate at which the decay will take place, and therefore the durability that may be calculated on, will vary very much with the nature of the material, the conditions to which it is exposed, and the care that is taken to protect it.

In many cases (*e.g.*, wood) decay is greatly accelerated, if not produced, by the action of living organisms, but up to the present these have not been proved to have any influence on the corrosion of metals, so that in this case it is purely chemical and physical changes that have to be considered.

The protection of structures is of the utmost importance, but in order that the protection may be satisfactory it is necessary that the conditions which tend to bring about the decay, and which, therefore, must be guarded against, should be known. A disease must be diagnosed before it is possible to prescribe for it.

THE AIR.

(1) Pure dry air consists, as is well known, of a mixture of oxygen and nitrogen, with certain other chemically inert gases (which have recently been

discovered, and which are of no importance from the point of view of corrosion) in the proportion of—

By volume	Oxygen	21	Nitrogen	79
By weight	„	23	„	77

the nitrogen in each case including the above-mentioned inert gases. These figures, however, do not represent the air as it actually is, but rather an ideal air, as it would be if all extraneous and accidental impurities were absent. Actual air, as it exists round about us, always contains (1) carbon-dioxide (carbonic acid gas); (2) water, in the form of water vapour intermixed with the air; and (3) various other gases in minute and variable quantity.

Carbon-dioxide is present to the extent of about '04 per cent by volume, or 4 volumes in 10,000 volumes of air—a quantity very small, yet sufficiently large to play a very important part in the phenomena of rusting. The quantity varies slightly under different conditions, but is so constant all over the world that carbon-dioxide must be regarded as being an essential and not an accidental constituent of air.

(2) Water is always present in the air, but in very varying quantity. Water gives off vapour at all temperatures, and it evaporates into the air exactly as it would into a vacuum, till the vapour exerts the pressure due to the particular temperature. Thus it displaces some of the air, and, according to what is known as the law of partial pressures, in a mixture of gases, each gas exerts exactly the same pressure as it

would if the other were absent. Air which is saturated with moisture may therefore be regarded as being a mixture of air and water vapour in proportions depending only on the temperature, and since water vapour is lighter, bulk for bulk, than air, air saturated with water is lighter, and therefore exerts less pressure than dry air.

At a temperature of 10 deg. Cen. (50 deg. Fah.), the tension of aqueous vapour is 9·14 mm., so that if the barometer stands at 760 mm., the relative pressure of air and water vapour, and therefore the relative volumes of the two gases, will be as 750·86:9·14, or the volume of water vapour will be 1·2 per cent., and the weight of water in the cubic metre of the air will be 9·3 grammes (or 4·16 grains in cubic foot). As the temperature rises, the amount of water which can exist as vapour in the air largely increases.

When the amount of water vapour mixed with the air is the maximum possible at that temperature, the air is said to be saturated with moisture, and under such conditions, if the air be cooled, the water being unable to remain in the gaseous condition will be deposited in the form of minute drops, which may, of course, collect into larger drops, and such deposition will usually take place first on the surface of solid bodies, which by their radiation become cool. If the cooling be general, a mist may form, or, if it be only local, dew may be deposited, and when the air is in contact with a cooled body moisture may be deposited on it.

When the amount of water vapour in the air is near the maximum possible at that temperature the air is said

to be wet, evaporation takes place very slowly, and any cooling will tend to deposit moisture; on the other hand, if the amount of water vapour be much less than the possible maximum, the air is said to be dry, because evaporation goes on very rapidly, and there is little tendency to deposit moisture. The temperature at which air under any given condition deposits moisture is called the dew-point. When the dew-point is near the actual temperature, the air is wet; when it is considerably lower, the air is dry.

The terms wet or dry as applied to air are thus quite independent of the actual quantity of moisture which may be present, a dry air on a summer day actually containing very much more water than a very wet air in winter.

When heat is spoken of as drying air, the term drying is being used in an unusual if not an incorrect manner, for the heated air is only drier than the cool air in the sense that it can take up more water, but if it be cooled again the water which is present may be deposited. On the other hand, cooling may actually dry the air by causing the deposition of the moisture as water, or, in cases of a very low temperature, as snow or ice.

The deposition of water on cold surfaces when the air is nearly saturated plays a very important part in the rusting of metals.

(3) In towns the air may contain other impurities; these are usually present in small quantity, so small as often to escape detection by the ordinary methods of analysis, yet in sufficient quantity to have important

effects on substances exposed to their action, and as these impurities are mostly soluble in water, they are dissolved out by the water which is condensed, or which falls in the form of rain, and are thus brought in contact with surfaces on which they may act.

The air is also laden with solid matter of various kinds held in suspension, which is slowly deposited, and which is washed out by the action of rain. In Glasgow the amount of solid matter deposited from 1st of March till the 8th of June, 1904, as a result of 25 tests in different parts of the city, was found to average 109·07 grains per square foot, which would be equal to 12·9 cwts. of solid material per acre per annum.

This 109·07 grains of solid material consisted of 3·56 grains of fatty material, soluble in ether, 41·89 grains of organic matter, and 63·62 grains of mineral matter. This solid matter probably has no direct action in producing corrosion, but it is more or less hygroscopic, and therefore tends to absorb water and thus keep the surfaces exposed to the air moist, thus greatly accelerating chemical action.

The action of atmospheric air, under various conditions, is now well known, and will be briefly described.

ACTION OF AIR ON IRON AND STEEL.

The ultimate product of the action of air on iron and steel is always a hydrated oxide of iron, and it is therefore evident that the oxygen must play an important part in the rusting.

Pure dry oxygen, and therefore pure dry air—since

the nitrogen is inert—has no action on iron at ordinary temperatures, though the action of oxygen is well marked at a red heat. Pure water—that is, water free from salts in solution and from air and carbon-dioxide in solution—also has no action, nor has carbon-dioxide alone or in presence of water only. These results, which have been proved by experiment many times, and which can be easily demonstrated, may be tabulated:—

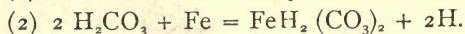
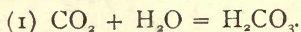
Action of water on iron.....	None.
Action of air on iron	„
Action of carbon-dioxide on iron	„
Action of water and air on iron	„
Action of water and carbon-dioxide on iron...	„
Action of air and carbon-dioxide on iron.....	„
Action of air and carbon-dioxide and water on iron,	Rapid rusting.

But even this last statement needs some qualification, for no rusting is produced even by the combined action of air, carbon-dioxide, and water whilst the water is kept in the condition of vapour, but it becomes extremely rapid as soon as any water is deposited in the liquid condition on the metal. Hence iron may be perfectly preserved by keeping it in a warm place, at a temperature well above the dew-point, so that no moisture can be deposited on it. It is not that water is not present, but that whilst it is in the condition of vapour it has no rusting action.

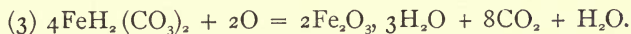
The rationale of rusting has now been well made out, and may be thus described:—

‘Metal being exposed to the air, and being a good

conductor and a good radiator of heat, cools rapidly, and as soon as it reaches the dew-point of the surrounding air water is deposited on it. The water, however, is not pure, but contains a small quantity of oxygen and of carbon-dioxide in solution. Carbon-dioxide dissolved in water forms a weak acid known as carbonic acid. This acid at once attacks the iron, forming a minute quantity of bicarbonate of iron (ferrous bicarbonate), which dissolves in the water. Thus



Bicarbonate of iron, like all other ferrous salts, is very unstable, and is easily oxidised to the ferric condition by oxygen, even at ordinary temperatures. It is therefore oxidised by the oxygen in solution in the water, and as no ferric carbonate exists, ferric oxide is formed, which, in combination with water, forms ferric hydrate, and the carbon-dioxide is liberated thus:—



The carbon-dioxide does not escape, but remains in solution in the water.

It will be seen, therefore, that the action is a cycle. It starts with iron and carbonic acid and ends with iron rust, and the quantity of carbonic acid unchanged still in solution, and ready to start its work over again. Thus a small quantity of carbon-dioxide can, if time be given, rust away an unlimited quantity of iron, and the amount of rusting is not proportional to the quantity

of carbon-dioxide present. The rusting will only cease when the supply of water fails to be kept up.

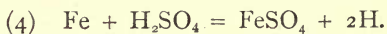
As already remarked, air ordinarily contains other substances in addition to water and carbon-dioxide. Town air always contains sulphur, in combination with oxygen, as sulphur-dioxide, which in contact with water forms sulphurous and sulphuric acids, chlorine as chlorides of sodium and ammonium, and nitrogen as nitrates and in organic combination. The sulphur compounds are, of course, mainly derived from the combustion of fuels containing sulphur, and the quantity is said to be much larger in towns where coals containing much sulphur are burnt than in other places. It should also be noted that these constituents are mostly soluble in water, and therefore largely brought down by rain or by water which separates from the air, the air being thus cleansed, but at the same time increased corrosive power being imparted to the deposited water.

Accurate analyses of the air of towns are not abundant; but about 25 years ago an exhaustive series of analyses extending over many years was made by the late Mr. E. M. Dixon, B.Sc., of the air of Glasgow, and these may be taken as being representative. He found, as might be expected, that the constituents present varied much, according to the weather and other conditions. The amount of carbon-dioxide was found to be less than that usually given (4 parts in 10,000), the average being about 3·5 parts in 10,000. The amount of combined sulphur (sulphur-dioxide and sulphuric acid) varied much, but may be taken as being about '5 mg. (0075

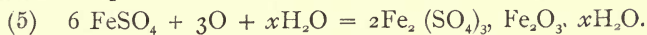
grains) in 100 cubic feet, and the amount of chlorine (as chloride) about '07 mg. ('001 grains) per 100 cubic feet.

These quantities seem exceedingly small, as indeed they are, and in ordinary analysis might be neglected, but when the enormous amount of air present is borne in mind, the constant change of the air in contact with any surface, and the long time over which the action goes on, it will be evident that their influence is not to be neglected. These figures relate to the open air; under some conditions, as in railway tunnels and other closed spaces, the amount of sulphur may be very much larger.

The action of sulphurous and sulphuric acids on iron is much the same as that of carbonic acid, except that the action is not of the character of a cycle, as the acid is not, or at least is only partially, released by the oxidation. In the case of sulphuric acid the action is: first, the acid forms ferrous sulphate with the iron, thus—



This is then acted on by the oxygen and water, forming a basic sulphate—



This basic ferric sulphate is an insoluble brown body, very like ferric oxide. With sulphurous acid the action would be very similar, the ferrous sulphite, if formed, being oxidised to ferric sulphate by the oxygen in solution, and finally a basic salt being formed. The action of chlorides and nitrates would probably be very small and somewhat uncertain.

Dr. R. M. Buchanan, bacteriologist to the city of Glasgow, has recently been studying the corrosion of stone in the city, and the results he has obtained show the presence of sulphur acids in the air, and the great influence they may have on any substance exposed. In one case a sample of stone contained '368 per cent of sulphate, but the surface of the stone where it had been subjected to atmospheric action, and was softened and decayed, contained 1'86 per cent of sulphates.

A mass of sooty matter that was found hanging as a sort of stalactite from the corner of a public building, and which had evidently been deposited from the air, was free from disintegrated stone, and consisted of—

 Volatile matter 35'76 per cent

 Mineral matter 64'24 ,,

and contained 31'46 per cent of sulphur as sulphates.

Iron rust is usually reddish-brown in colour, though it may be almost, or quite, black, the colour depending largely on its physical condition, and to some extent it is modified by the impurities that may be present. It consists mainly of the iron combined with the oxygen and water taken up, forming a ferric hydrate, but it may be contaminated by the presence of dust deposited from the air, and in the case of surfaces originally painted or otherwise protected, with the remains of the protecting material.

The following analyses of iron rust, made many years ago by the late Dr. F. Grace Calvert, are usually taken as being typical examples. They are from the Conway and Llangollen bridges, and therefore represent the rust

formed in comparatively pure air. The samples were, of course, dried before analysis:—

	Conway Bridge.	Llangollen Bridge.
Ferric oxide (Fe_2O_3).....	93'094	92'900
Ferrous oxide (FeO).....	5'810	6'177
Ferrous carbonate.....	'900	'617
Silica	Trace.	Trace.
Calcium carbonate	—	'295

The ferrous oxide may be present as free ferrous oxide, but more probably is in combination with some of the ferric oxide forming the black or magnetic oxide. If the latter be the case, the figures would be:—

Ferric oxide (Fe_2O_3).....	80'322	79'174
Magnetic oxide (Fe_3O_4).....	18'719	19'903

The ferrous oxide may be, and probably is, due to incomplete oxidation of the ferrous carbonate, or it may be due to subsequent reduction by the action of organic matter from the paint, or from dust, or by the hydrogen evolved by the solution of the iron.

When the rust is obtained from towns where there is much sulphur in the air, it invariably contains traces of sulphuric acid.

Three samples of rust taken from buildings in Glasgow were found by the author to contain:—

	No. 1.	No. 2.	No. 3.
Ferric oxide	95'34	93'98	96'44
Ferrous oxide	3'94	5'38	1'86
Sulphuric acid (SO_3)	'72	'64	1'70
	<hr/> 100'00	<hr/> 100'00	<hr/> 100'00

No carbonic acid being detected in any of the samples.

The usual phenomena of the rusting of iron may now be quite well explained.

As is well known, iron or steel never rusts evenly over the whole surface of the metal which is attacked, but the rusting begins in spots or isolated patches, from which the rust spreads until the whole surface may be covered, each spot, therefore, being a centre of corrosion. As the rusting spreads not only laterally over the surface, but downwards into the metal, when the rust is cleaned off, the surface below is never smooth, but is eaten out into pits of greater or less depth and area, each pit indicating a centre of rusting, the depth of the pit depending on the extent to which rusting has gone on.

Each centre of corrosion is a spot at which for some reason or another water has been deposited in the form of drops, or, if the metal has been completely covered with water, it may be the spot from which the water last evaporated, and, therefore, where a liquid drop remained the longest time. At these spots rusting will continue as long as there is moisture present, for the carbon-dioxide liberated will re-dissolve in the water, as already explained, and continue the action.

As ferric hydrate is very hygroscopic—that is, tends to absorb water from the air and to become wet—it will remain damp whilst there is moisture in the air, even though the air be not nearly saturated, and thus the rusting may continue even when the surrounding portions of the metal are dry. When, for any reason, the whole surface becomes dry, the action will cease, only to be resumed as soon as moisture is re-deposited on it.

from the air or otherwise. Even if the rust be completely cleaned away, the surface beneath is left rough and more or less porous, just in the condition favourable to receive a deposit of moisture from the air, and therefore rusting may start again at the same spot if the conditions be otherwise favourable. Not only, therefore, is a layer of rust no protection, as it is sometimes alleged to be, but, on the contrary, it accelerates further rusting, and the rusting may go on until the metal is completely destroyed. Sometimes the metal may retain its form to the end, but more usually it will fall to pieces, the rust formed not being adherent to the metal, and falling off in flakes or masses.

It is quite obvious from what has been said that rusting must take place on iron or steel surfaces exposed to the air and moisture in such a climate as this, unless they be well protected, and even with the best protection that can be given their complete destruction can only be a matter of time.

The climate to which iron or steel is exposed will, of course, have great effect on its durability. In warm dry climates, even where there are periodical rains, the metal may stand well. In India, for instance, there is ironwork thousands of years old freely exposed to the air, but in a climate such as this, where the air even in fine weather is always damp, and where rain is so frequent, corrosion is very rapid, so rapid that examples may be seen on every hand by those who take the trouble to look for them.

The durability of an iron structure will depend largely

on its mass, if the rusting be at all uniform, for the greater the mass in proportion to the surface exposed, the longer it must take, other things being equal, for corrosion to destroy it. A thin plate may be rapidly eaten away, but the same amount of corrosion on a thick plate or large mass would not appreciably reduce its strength. It must be remembered that the strength of a structure, whether measured by the stress it will bear or by its resistance to corrosion, is only the strength of the weakest member, so that an average is of little use. Unfortunately, also, the decay of iron and steel is so erratic that it is impossible to form an idea of the probable durability of a structure from the average rate of corrosion of the metal, because one portion may be far gone with rust, whilst other portions may be sound and strong, even though the two portions may seem to be under exactly similar conditions. Some, apparently accidental—that is, unforeseeable—circumstance having caused rusting to start in one place, it will go on increasing, as already explained.

The main point to be guarded against in all iron or steel structures is to prevent the deposition of water, for, as pointed out, it is this that starts corrosion, a wash of rain running over the surface being far less objectionable than the deposition of water in drops, or in a film over the surface.

It follows that every part of the structure should be exposed to the free circulation of air, so that water deposited may evaporate as quickly as possible. If there is any portion where there is not this circulation,

moisture is sure to accumulate, and rusting will become rapid. Every part of the structure should also be easily accessible on all sides for examination and painting. The custom, unfortunately too prevalent, of putting iron girders and other members in positions where there is no circulation of air, and where they are not accessible to inspection, must sooner or later lead to disaster.

All iron structures should be protected from dripping water, for this will almost certainly lead to corrosion, and there should be no places on which water can lodge. All flat parts, therefore, should be made perfectly flat, so that there are no depressions in which water can rest, as water will find its way into every crevice that is left, however small. It may find its way in behind rivet heads, into the rivet holes if the rivets do not completely fill them, in between plates of metal supposed to be in contact or riveted together, and as such places are not exposed to an air current evaporation will not go on, and the rusting will probably be rapid. In riveted structures the decay of the rivets is one of the great dangers, because it can go on entirely unnoticed. The loss of a few rivets may not endanger the structure, but if the decay becomes general it must be a source of serious weakening. Therefore, all rivets must completely fill the holes, and all heads should be pressed up so firmly that there is no possibility of moisture getting in (for this reason hydraulic riveting should be used wherever possible), and similarly all jointed parts must be in absolute contact. The closer the riveting the better, because the better will the plates be kept in contact.

In illustration, the following quotation may be of interest: "The majority of bridge members, indifferently closed by rivets, are unpainted on their inner surfaces, and are of such construction that it is now impossible to coat their inner surfaces even by the action of a force pump. Hundreds of minor parts are painted in so careless a manner that the protective coating is but little better than a wash of brickdust, the curdled appearance of some of the coatings clearly indicating that the red lead paint had set before its application, and that the pigment is of an inferior quality. The greater part of the steel work is to be placed where it will be always damp, and so walled in as to be inaccessible for inspection, or else exposed to an atmosphere always charged with tunnel vapours."

Speaking of the Forth Bridge, the same writer says: "Thousands of rivets, many of them 1'25 in. to 1'5 in. in diameter by 9 in., will be so corroded under their heads as to have lost their set. In fact, the stability of the bridge in future will rest quite as much upon its mass as upon the mutual strength of its connecting members."

Exposure to foul gases, such as tunnel gases, etc., is a very prolific cause of decay, and iron in such positions needs very careful protection.

Exposure to dirt and deposited solid matter will greatly facilitate corrosion, as this is frequently very hygroscopic. Not only so, but the smoke or soot of which it is largely composed in towns or other smoky places generally contains a considerable quantity of

sulphuric acid, the action of which has already been discussed.

Contact with any hygroscopic substance is, of course, objectionable, and therefore contact with wood, unless this be well painted so as to prevent the absorption of moisture; but even then the wood may decay, and the products of its decomposition act injuriously on the metal.

Sea spray or salt water is a very rapid corroding agent, not so much from any direct action which it has, as because the salt (sodium and magnesium chloride) is very hygroscopic, and, therefore, keeps the surface continually wet.

The part of a structure which will be the first to give way is, of course, very uncertain, owing to the different conditions under which the various parts will be placed and the relative thickness of the various parts. Owing to the influence of mass, small or thin parts are liable to go first. The heads of rivets very frequently rust away, owing to moisture getting in behind them, and other small members corrode away rapidly, and unfortunately the stability of a structure is often very largely dependent on these small parts. In a girder the web, being much thinner than the flanges, is very apt to be corroded through, and in general the small and thin parts need special attention.

CHAPTER II.

PROTECTION OF IRON AND STEEL FROM ATMOSPHERIC CORROSION.

THE only way in which corrosion can be prevented is by preventing the access of the corroding agents to the surface of the metal. Theoretically this may be done in two ways: (1) By purifying the air which comes in contact with the metal from these substances; and (2) by covering the surface of the metal with some substance which is impervious to them.

In practice, except in a very limited number of cases, such as the preservation of small articles by packing in lime, the former method is impracticable, and we have to fall back on the latter as being the only possible means of protecting a metallic surface from corrosion.

Five methods of coating the surface for this purpose are in use:—

- (1) Covering the surface with a layer of another metal;
- (2) Covering the surface with a metallic oxide;
- (3) Covering the surface with a layer of paint, varnish, or bituminous (or other) composition;
- (4) Covering the surface with a porcelain enamel;
- (5) Covering the surface with a layer of cement or similar substance.

In order that a covering of any kind may be a satisfactory protection it is necessary that—

- (1) It should be impervious to air and moisture;
- (2) It should be of such a character that should the surface be broken through the covering material will not accelerate corrosion;
- (3) It should not be liable to be chipped or broken through by any treatment which the article covered is likely to receive in work or use;
- (4) It should be durable, and should not become porous, brittle, or cracked by the action of air, moisture, or light, or under the conditions to which it is likely to be exposed;
- (5) It should not of itself produce any deterioration of the metal to which it is applied;
- (6) It should be easy of application;
- (7) It should be easily renewable should the surface be broken or damaged by accident or otherwise.

No known material has all these qualifications in the highest degree, some which possess one or more of the qualifications in a high degree being very deficient in others. The selection in any particular case will usually be of the nature of a compromise, so as to obtain the object which is considered to be of greatest importance in that particular case as completely as the conditions will permit.

METAL COATINGS.

These are largely used for some purposes, and within limits are efficient. The metal may be applied in the molten condition by dipping the article into it, either

whilst in the sheet or in the finished form, as the case may be, or it may be applied in some other way, or it may be deposited from solution by means of an electric current. Electro-deposited metals form a layer on the surface, but do not, as a rule, form an actual alloy with the underlying metal, and, therefore, they frequently lack adhesive power, and are more or less readily chipped; and at the same time are frequently so porous that air and moisture find their way more or less readily through the layer, which, therefore, has little protective power. There are, however, marked exceptions to this.

When the metal is coated by dipping or passing through a bath of the molten protective metal, an alloy is usually formed, which passes inward into the metal and outward into the coating, so that there is a gradual passage of the one into the other, and not a hard and sharp line of demarcation between them. Such coatings are, therefore, very firmly adherent, and are not liable to chip.

The metals usually used as a protective coating are tin and zinc, and for some purposes copper, nickel, and brass. Gold and silver are also used, but only for purposes of ornament rather than protection from corrosion.

TIN,

This metal is largely used in the preparation of tinplate. Sheets of mild steel (Bessemer or Siemens) are cleaned, and are then tinned by being dipped into or passed through a bath of molten tin. The tin alloys with the iron, and forms a perfectly adherent coating of

metallic tin, which is bright and lustrous. The layer of tin is so malleable that it does not readily crack, and, therefore, the plates can be used for making up articles of various kinds, such as cooking and other utensils, without fear of cracking the metallic surface. The tin surfaces are also easily united by means of solder, which alloys readily with tin. Metallic tin is, however, readily attacked by corroding agents; and, being electro-negative to iron, once the surface is broken through, electric action is set up, which greatly accelerates the corrosion of the iron; and as any joints in the articles are made with solder, this may be rapidly attacked. For these reasons tinplate is only used for the manufacture of small articles, mainly for domestic use, and never for structures which have to be exposed to the weather, and in any case the protective power of the tin is very small.

ZINC.

Galvanised iron—that is, iron or steel coated with zinc—is very largely used for structural and other purposes, and is very useful, since under some conditions zinc affords excellent protection. When any large amount of work, such as bending or riveting, is to be put on the metal in making it up to the required form, the article is usually galvanised after it is made up, as the zinc coating might crack under work, it being too brittle to stand very rough usage. Zinc is readily acted on by acids and alkalies, but resists the ordinary atmospheric corrosive agents in the air very well. It is

electro-positive to iron, so that should the surface be broken through and galvanic action set up, the zinc will dissolve and will protect the iron till it is completely removed.

Iron is usually galvanised by dipping the article into or passing it through molten zinc, after the surface has been thoroughly cleaned. It is quite obvious that articles of very large size, and structures which have to be erected outside, cannot be galvanised as a whole, but various parts or members can be so treated separately, and then riveted or otherwise fixed together, if proper precautions are taken to avoid breaking the surface of the zinc.

For internal work galvanised iron stands excellently, and for outside work in the purer air of the country it is very durable, galvanised-iron buildings standing for many years without any sign of corrosion. In towns, on the other hand, where the air is loaded with sulphur acids, it cannot be depended on to resist corrosion for any length of time.

As by the ordinary process the articles are dipped in molten zinc, articles which might be warped or otherwise injured by heat treatment cannot be galvanised.

Galvanised articles are quite unsuited for domestic use, as the zinc is attacked by acids and by alkalies, and when brought into contact with soap the soap is decomposed, and the zinc becomes covered with a layer of a sticky zinc soap.

With all its faults, galvanising is a most useful method of protection, and is not as much used as it might be. Under a good coat of paint it gives an additional

protection, and in the future it is likely to be far more used than it has been in the past, as with improvements in the details of galvanising, and a better knowledge of the conditions required for protection, better work is being turned out, and good galvanising will compare favourably with most other methods of protecting iron surfaces, the one great defect being that it is impossible to renew it.

Zinc may be deposited in other ways where the hot galvanising or dipping is impracticable. In the "Sherardising" process the article is heated and agitated with zinc powder, by which means a dead grey layer of metallic zinc is deposited on it. The author has no data as to the durability or protective power of the zinc so deposited, but some experiments he has made seem to indicate that it is as durable as zinc applied in the ordinary way.

Zinc may also be deposited by the electrolytic, or wet galvanising process, which has been made a success by Mr. Sherard Cowper Coles. This process is now largely used, especially for articles for which, for various reasons, the hot process is inapplicable. Here again the author is without definite data as to the protective value of such a coating.

On the whole, zinc is the best of all the metallic protective coatings, and is very largely available.

COPPER AND NICKEL.

Copper and nickel, electro-deposited, are used for the protection of small articles. The protection afforded is



slight, as the deposited metals are so porous that air and moisture readily penetrate them, and, therefore, rusting may go on beneath the surface. In the case of copper this difficulty may be overcome by burnishing, by which the crystals of the metal are pressed into contact, and the metal is rendered denser and more impervious; but electro-deposited nickel is too hard to allow of this. For iron or steel bicycle fittings and similar articles a layer of copper, well burnished, and then covered with a layer of nickel, is an effective protection, but without the burnishing the layer of copper under the nickel is of little use.

Electro-deposited brass is mainly used for ornamental purposes.

OXIDE COATINGS.

The only "oxide-coating" process which is used for the protection of iron and steel is that known as "Barffing," which was invented by Professor Barff in 1876. In the form in which it is now used this is commonly called the Bower-Barff process, and is a combination of that of Professor Barff's, with a modification patented a year later by Mr. Bower.

The articles to be treated are cleaned, and are then heated in a closed chamber in a reducing atmosphere by means of producer gas; the gas is then turned off, and superheated steam is sent through the chamber for one or two hours, and the articles are left to cool. When removed from the oven they are coated with a dull, dark grey, or black film of magnetic oxide of iron, which, whilst it remains unbroken, is a perfect protection

against rust. It is, however, very brittle, so that the article after "Barffing" must not be subjected to much work or rough usage. The process is very valuable for the protection of small articles of various kinds which have to be subjected to the influence of air and moisture, but obviously it can only be applied to articles small enough to go into the furnace, and which will not be injured by the high temperature to which they will necessarily be exposed. The process can be used for cast iron, malleable iron, or mild steel, a lower temperature being used for the first than for the others.

PAINT AND VARNISH.

The most general method of protecting metallic surfaces is by coating with paint or varnish of some kind. This is applicable under almost all conditions, and under many it is the only method which can be used. It has some advantages and many defects, and will need a more full discussion than the previously-described methods. If an article is to be tinned or galvanised, once the method is selected, the tinning or galvanising will be left in the hands of the manufacturer whose business it is to carry out these processes. On the other hand, if the structure is to be painted, the painting will be done under the supervision of the engineer, who will be responsible for it. And as the preservation of a structure is almost as important as its erection, too much care and thought cannot be given to the details of the protection on which this preservation so largely depends.

It will be well, therefore, to consider first the materials used, and then the methods of using them, so as to obtain the best results, for it must be remembered that the best results can only be obtained with good materials carefully and skilfully applied, and that even the best materials will be of little avail unless they are so used; indeed, poor materials used with skill will often give better results than the best used without skill or care. The painter who is painting a structure for its preservation, just as much as an artist, requires to mix his colours "with brains."

Under the general term paints and varnishes are included, for convenience, four groups of materials which have much in common, but many differences both as to the purposes for which they are used and the method of using. It is impossible to draw a hard-and-fast line of demarcation between the various materials, but the following classification, while not in any sense scientific, will be practically convenient:—

(1) *Paint*.—A mixture of a solid material or body, with a drying oil, with or without the addition of other materials for imparting colour and for diluting the mixture to a suitable consistency for work.

(2) *Varnish*.—A solution of gums or resins in a volatile solvent, so that when it is spread over a surface the solvent evaporates and leaves a layer of the gum or resin, which forms the protective layer, or a solution of gums in drying oils.

(3) *Bituminous Compositions*.—These are mixtures of various materials, of which tar or pitch usually forms

a large proportion, they are melted, and into them the article to be protected is dipped. Enough of the mixture adheres to the surface to form, on cooling, a solid protective layer.

(4) *Oil and Grease Coatings.*

PAINT.

A paint, as already remarked, consists essentially of two parts—the vehicle and the base—to which in general other substances are added for various purposes. For paint, considered as a protective agent where colour is of little importance, these two constituents alone are essential, and the addition of others should be avoided as far as possible.

The vehicle is almost always linseed oil, and for protective painting no other oil should be tolerated. Linseed oil, as is well known, is obtained from the seeds of the flax *linum usitatissimum*, which is cultivated in various parts of the world, not only for the seeds from which the oil is obtained, but also for the fibre.

Linseed oil is the best of the drying oils, and a drying oil of some kind is essential as a vehicle for paint. All oils are more or less acted on by oxygen on exposure to the air, and according to the nature of this action they are classified into non-drying and drying oils.

The non-drying oils and fats are more or less oxidised, yielding various products which have an unpleasant odour, so that the oils are said to become rancid, and which also have an acid reaction. The drying oils, on the other hand, absorb oxygen, and are oxidised into solid

more or less resinous semi-elastic transparent substances. In the case of a mass of oil the change takes place first at the surface, and then only very slowly, since the oxidised material is nearly impervious to air, though ultimately the whole mass may be oxidised, but in the case of a very thin layer oxidation quickly takes place through the whole thickness. It is on this oxidation that the drying of a paint depends. It is a direct oxidation, due to the action by the air, and is not, therefore, greatly facilitated by heat, though, like almost all chemical changes, it is somewhat accelerated by heat.

The body formed by the oxidation of linseed oil is known as linoxilin. It is quite neutral in its reactions, somewhat elastic, nearly transparent, and it is insoluble in water, alcohol, or ether, and only slightly soluble in chloroform; hence, when once a paint has hardened, it is difficult to remove by chemical means. It is, however, attacked by a hot solution of caustic potash.

The value of linseed oil for painting purposes depends on the speed with which it will "dry," or, to put it in other words, the rate at which it will absorb oxygen from the air. And this is greatly increased by heating the oil to a moderate temperature—the best being from 400 deg. Fah. to 500 deg. Fah.—for some hours before use. Oil which has been so treated is called boiled linseed oil, and is generally used for paint making. If the temperature of "boiling" be too high, the oil becomes much darker in colour.

The absorption of oxygen, and therefore the drying, can be greatly accelerated by the addition of certain

substances—technically called driers—which seem to act as carriers of the oxygen from the air to the oil. Of these substances the best known and most used are red lead and litharge (the former being the better), manganese dioxide and other lead, manganese or zinc salts. The many patent driers are mostly mixtures of some of these with other substances. The character of the drier and the quantity used may have considerable influence on the quality of the paint, and, in general, for protective purposes the less used the better.

Like all natural products, the quality of linseed oil may vary very much, and the qualities depend largely on the localities where the flax is grown. Of the oil that comes to British markets that from the Baltic is considered to be the best, and that from the Black Sea to be next, whilst the East Indian is regarded as being of inferior quality. Oils are also brought from other localities in smaller quantities, but it is impossible to place them according to their quality.

It is not necessary to discuss here the properties of the varieties of linseed oil, for which the reader can refer to the books dealing specially with oils, since the tests required to determine the purity and quality of the oil can only be made by a chemist with proper laboratory appliances. Whilst the purity of the oil is of great importance, the most important property for paint making is the rate of drying and the character of the film left, and these can be ascertained by spreading a thin layer of the oil on a sheet of glass and leaving it exposed to the air till it has hardened.

Since linseed oil is not only the best but the most costly of the drying oils, it is sometimes adulterated with the cheaper oils, such as poppy seed oil, etc.; also various fat oils, such as cotton seed oil, rosin oil, and mineral oils, all of which are very objectionable. Substitutes for linseed oil are sometimes used, and whilst they answer well enough for some purposes, they are always inferior to the genuine oil, and should never be used where the oil is used for making paint for protective purposes.

For temporary purposes linseed oil alone is sometimes used for a protective coating, and it answers fairly well for the purposes for which it is usually used, but it is of little use as a protection against atmospheric corrosion, since as the oil dries the layer of linoxylins which is left is more or less friable and cracks considerably, so that air and moisture readily find their way through and corrode the metal beneath.

It is on account of this property of the dried oil that some solid material or base is always mixed with the oil in the preparation of paint, so that the dried layer consists of a film of dried oil uniting the solid particles of the base, and there are, therefore, no large areas of dried oil to contract and crack. The base adds very much to the protective power of the paint.

Where a paint is to be used not merely for protective purposes but also for ornament, a pigment or colouring matter is also added, and it is obvious that this must either be also the base, or that the base must be white. For coloured paints, therefore, the base is almost always

white lead, "a basic carbonate of lead," or some other white body, such as zinc oxide or barium sulphate.

For protective painting colour is of little moment, and that base should be selected which will give the best protection, and at the same time will be the most durable.

The bases most generally used are white lead, red lead, and red oxide of iron, whilst black oxide of iron, graphite, and silica are used more rarely.

The base must be of such a character that, with the oil, it will form a layer impervious to the action of the atmospheric corroding agents, which have been already described, and it must, therefore, not be acted on by them in any way; it must also unite well with the oil, not only in the liquid condition, so that it may flow freely and be evenly spread, but also when the oil has hardened, and it should expand and contract as nearly as possible at the same rate as the dried oil. The base will, of course, be more or less completely enclosed in the dried oil, but the protection given in this way is by no means complete, as is shown by the way in which atmospheric influences change the colour of many pigments. It is sometimes stated that the base should be of such a nature as to absorb moisture from the surface to which it is applied, though when once dry it must resist the action of water. It is difficult to see that this, even if it could be obtained, would be any great advantage.

The value of the base will depend both on its chemical characters and on its physical condition.

WHITE LEAD.

White lead has many advantages as a base which have led to its being very largely used. It mixes well with oil, has a considerable covering power, and, being white, pigments of various kinds can be mixed with it. For protective paint it is, however, quite unsuited. Like all carbonates, it is more or less readily acted on by acids, and, as has been already pointed out, there are always acids in the air of towns, and even the carbonic acid, which is present in air everywhere, will slowly attack it, dissolving it away. The most marked action of the air of towns on white lead is the blackening which goes on under the influence of the sulphur compounds, owing to the formation of lead sulphide.

The use of white lead in any form should be absolutely prohibited in paints for use on structures exposed to wet and impure air. If a white base must be used, there are several others available, and zinc white is probably the best. If white lead be used, care must be taken that it is pure, as it may be adulterated with other carbonates, such as carbonate of lime, and with other substances, which may very considerably reduce its power of resisting the destructive action of the air.

RED LEAD.

This oxide of lead, to which the formula Pb_3O_4 is usually given, is a dense powder of a bright red colour. It is very largely used as a base for paints to be used for protective purposes; indeed, it is probably the most popular of all the bases for this purpose. Its qualities

for this purpose are, however, much over-rated. Like most lead compounds, it combines with the oil, and, owing to its oxidising power, it produces very rapid drying, so that red lead paints dry more rapidly than most, and this no doubt is an advantage under some circumstances, especially for shop use. On account of this action red lead may be used with raw oil. Whilst red lead is little acted on by the ordinary atmospheric corrosive agents, it has been shown by experience to fail as a protection against corrosion. Lead paints are frequently very brittle, and very often crack and break away from the metal.

IRON OXIDES.

There are two oxides of iron which are used as the bases for paints—the red oxide Fe_2O_3 and the black oxide Fe_3O_4 . The former is the more frequently used, and is what is commonly meant when an iron oxide paint is spoken of. The red oxide is a red powder, the colour varying very much according to its purity and the way in which it is prepared. It is lighter than the lead compounds, and does not incorporate so readily with oil, so that a larger proportion of oil is necessary in the paint. It has no chemical action on the oil, so that it does not act as a drier, and it is quite inert under the influence of ordinary atmospheric corroding agents, and it has no action on iron. It is therefore one of the best, if not *the* best, material that can be used as a protective paint.

Iron oxide paints are largely used, and sometimes they are successful and at other times the reverse, this

depending largely on the purity of the oxide used. The iron oxide may be obtained in two ways: (1) By the grinding of the natural oxides which occur abundantly in various parts of the world; and (2) from iron compounds either by wet or dry processes. It does not seem to be of much importance which variety is used, but unless care be taken in selecting the material the natural oxide may contain impurities which will very seriously impair its resisting power. Much of the red oxide paint that is made contains various materials mixed with the oxide of iron. These may have little ill effect when the paint is required for ordinary purposes, but where it is to be used for the protection of ironwork only the very purest oxide of iron should be used.

Mr. Hurst, in his excellent book on "Painters' Colours," etc., to which the reader who desires more information on these points should refer, gives a table of analyses of red oxide of iron pigments, from which the following figures are taken:—

	1	2	3	4	5	6
Ferric oxide (Fe_2O_3)	96.00	94.71	98.5	9.60	92.72	5.17
Alumina (Al_2O_3)	1.24	1.6	—	1.42	—	5.05
Silica (SiO_2)	1.49	2.8	1.2	9.28	1.36	4.46
†Calcium carbonate (CaCO_3)...	—	.39	—	80.04	—	62.55
†Calcium sulphate (CaSO_4)	—	—	—	.10	5.52	1.00
Barytes (BaSO_4)	—	—	—	—	—	—
Water, combined	1.35	.69	.3	—	.39	20.14
†Water, hygroscopic	—	.14	—	—	—	.50
Organic matter	—	—	—	—	—	1.00
	100.08	100.33	100.00	100.44	99.99	99.87

No. 1, Natural hæmatite. Ulverstone. No. 4, Red chalk, Speeton, Yorkshire.
 No. 2, Natural Indian red from India. No. 5, Indian red.
 No. 3, Purple oxide. No. 6, Venetian red.

The following is an analysis published some years ago of a paint sold as pure oxide of iron paint, and which failed completely as a protective agent:—

Oil and volatile matter	13·35
Oxide of iron.....	4·85
Barium sulphate.....	57·95
†Calcium carbonate.....	18·77
†Calcium sulphate	4·17
Alumina.....	·67
	<hr/>
	99·76

The specially objectionable constituents are marked thus †. Calcium carbonate is soluble in water containing carbon-dioxide; calcium sulphate is soluble in water. These, therefore, will be dissolved away, as the continuity of the paint will be broken up, so that air and moisture can find access to the metal and rapidly corrode it. It is quite obvious that such paints as that in the last analysis, or made from such pigments as Nos. 4, 5, and 6 in the table, could not be durable. A good oxide of iron paint will adhere firmly, and show little tendency to peel off, but that this may be the case the pigment must be pure. An oxide of iron for paint should be specified to contain not less than 95 per cent of ferric oxide, and to be quite free from calcium carbonate, calcium sulphate, and hygroscopic water, and any sample containing more than a few tenths per cent of any of these should be rejected.

Fe_3O_4 has also been used, and forms a very durable protective paint of a black colour.

CARBON.

Carbon has been used under various circumstances, and, of course, yields a black paint. Whilst carbon is not acted on by the atmospheric oxidising agents, carbon paints are frequently non-cohesive, and are easily removed.

The only form in which carbon can be used satisfactorily for a protective paint is that of graphite. Graphite is perfectly inert to the ordinary corroding agents, not being acted on by air, water, or acids. It also mixes well with linseed oil, and forms a firmly adherent coating, which acts as a perfect protection. As the graphite is the important constituent, it is essential that this should be pure, and the natural graphite may contain anything from 20 per cent or even less up to 100 per cent of actual graphite, though the natural mineral rarely, if ever, approaches to the actual purity which would be indicated by the latter figure. Of fifteen samples of graphite from various localities, given by Dana as typical, only four contain over 90 per cent of graphite, the highest being 94·03 in a sample from the Urals, and the lowest 59·67, in a sample from the Alps. It is quite obvious that the quality of the graphite used is of the utmost importance. A real graphite paint, made with pure linseed oil and a graphite containing, say, 90 per cent of carbon, will be an excellent protective paint, whilst one with, say, a graphite containing 40 per cent of carbon will be almost useless, especially if a poor quality oil be used. In specifying such a paint, therefore, the purity of the graphite should be insisted

upon, and graphite paint should never be purchased from a maker who will not give the required guarantee.

Graphite paint has a dark steel-grey colour, which may, of course, be modified by the addition of other pigments, but the graphite alone will always be the most satisfactory.

MECHANICAL PREPARATION.

The material to be used as a base must be finely ground; indeed, the finer it is the better, and the particles must be very uniform in size, and very thoroughly mixed with the oil. It is, of course, the business of the paint maker to secure these conditions, and good paint can generally be relied on to be suitably ground and mixed. As a rule, little fault is to be found with paints on these grounds, but any paint that shows lumps of solid material should be rejected.

PAINT.

The paint will consist of the oil and its base thoroughly mixed together. It must be quite free from acid—either traces of mineral acid left after purification of the oil, or of organic acids produced by the oxidation of non-drying oils present.

Under no circumstances should paint to be used for protective purposes be purchased merely by name, but the composition—both as to the quality of the oil and of the base—should be specified by the engineer, and samples should be regularly analysed to see that the material supplied is in harmony with the specification.

In this, as in many other cases, a good specification is quite useless unless the engineer sees that it is adhered to.

The actual price of the paint should be of little moment compared with its quality. Low price almost always means poor quality, and low-priced paints are often the most costly in the end.

A suitable paint having been secured, great care must be taken in its use. Wherever possible, if it needs dilution, raw linseed oil should be used rather than turpentine, to bring it to the required consistency, and care must be taken by shaking and mixing that every portion drawn from the tins and used is of uniform composition. The careful painter will, of course, not neglect these precautions, and the careless man should never be employed for protective painting.

It is evident that, as paint hardens from the surface, and as the hardening can only go on as oxygen can reach the oil, the thicker the layer of paint and the more impervious it is to air, the longer it will take to harden. It follows that the paint should be put on in thin even layers, each being allowed to harden before the next is applied; and also that any irregularities, such as streaks, or drops where the paint is much thicker, must be carefully avoided, as the hardened surface of such spots may be lifted away during the application of the next coat, or by handling. In general, three coats of paint should be applied.

The durability of paint depends on many conditions, but under any circumstances its life cannot be very long. The hardening of the oil is an oxidising action, and

when the hardening is completed the oxidising will not stop. All organic materials, without exception, are oxidised and broken up under the influence of air, light, and moisture, and linseed oil, being an organic substance, must share the same fate. The hardened oil gradually becomes more and more oxidised, breaks up into a pulverulent mass, and ultimately falls to powder. The body, if it be of suitable material, will not be acted on, but it will to a large extent fall away with the decaying oil, though portions may remain adherent for a long time. The decayed paint will probably partly fall away and partly remain adherent in ragged masses; but long before the point of complete destruction is reached it will have become porous, water and carbon-dioxide will find their way through, rusting will go on beneath the surface, and the paint may be thrown off in large or small flakes by the increase of volume of the rust beneath.

The principal agents which aid the destruction of the oil are oxygen and sunlight, and paint exposed to these conditions will be destroyed much more rapidly than that in places more or less protected from the light, the conditions in the two cases being very different. Physical conditions may also modify the durability. On a structure exposed to considerable vibration the paint tends to crack off, since the layer of dried oil is only slightly elastic, and therefore its surface may be readily broken.

In general, a coat of paint cannot be expected to exert any protecting action for more than two or three

years, and important structures should be re-painted every year, or at least every second year. An examination of a structure that has not been re-painted for over two years will almost certainly reveal indications of rusting in places.

VARNISHES.

Varnishes are of two kinds: Oil varnishes, in which linseed or other drying oil is associated with certain gums or resins, and spirit varnishes, in which the gums or resins are dissolved in volatile liquids, such as alcohol or turpentine. The former closely resemble paints in their constitution, and harden in much the same way, the gum serving as the "body." With the latter the solution is spread over the surface, and the "spirit," volatilising, leaves a layer of the gum or other material that has been dissolved in it.

It will be seen from what has previously been said the linseed oil itself might be regarded as a varnish, but neither it alone or associated with gums is of much value as a protective agent for iron, and of still less value are the ordinary spirit varnishes. They all tend to crack and break up on exposure to the air and sunlight, thus allowing air and moisture to find their way beneath them, and most of the gums are very rapidly broken up and softened under the action of air, moisture, and light.

Varnish paints, as they are called, are, however, frequently used for protective purposes, and also certain mixtures which might be included under the general terms of varnishes. Varnish paints are made by incor-

porating a base of the ordinary kind with a "spirit" varnish containing gum dammar, gum juniper, or other suitable gum. Such a paint, when dry, will, therefore, consist of particles of the base bound together in a layer of gum instead of in the dried linseed oil. Such paints are easily applied, dry quickly, and look well, but their durability and protecting power are uncertain, and the author would not rank them high.

BITUMINOUS VARNISHES.

Many black compositions, which may be considered either as paints or varnishes, because they are applied in a similar way, are largely used, and have very considerable success. Many of these are secret mixtures, whilst the composition of others is well known. They are almost all made from tar, pitch, bitumen, or similar materials, usually dissolved in the volatile distillates obtained in the distillation of coal tar. "A black varnish made on Dr. Lunge's method is declared to be excellent for iron. It is made by distilling gas tar until nearly all the volatile products are expelled. The residual pitch is then dissolved in the heavier oils, or, if a very quick-drying varnish is required, in light oils or naphtha. This varnish is the original tar without the ammonia, water, carbolic acid, etc., which cause it to have a disagreeable odour and to be so long before it is dry or hard." *

Solutions of pitch in various oils may be used. If the solution is thin and the oil volatile, it may be applied

* Newman's "Corrosion of Metallic Structures," page 303.

cold, but if thick it must be used hot. Tar thinned with a suitable oil or spirit, either a mineral or a naphtha, may be used, and answers fairly well for some purposes, but cannot be depended on as a protective agent.

Black varnishes or enamels consisting of natural asphalt or similar materials, either alone or mixed with other substances, and dissolved in oil or some volatile spirit such as coal tar or other naphtha, are largely used. These may either be in the form of enamels, which require artificial heat to harden them, or they may be in the form of varnishes, which will harden on exposure to the air. The former variety is largely used for coating small articles of ironwork, and it dries with a smooth lustrous surface, but obviously is only applicable to articles that can be "stoved."

The latter variety may be so made as to be applied hot, or it may be applied at its ordinary temperature. Many formulæ have been published for the manufacture of such varnishes, in which asphalt and other gums are mixed with oil, sometimes with the addition of red lead to promote drying, and then with a considerable quantity of turpentine to serve as the volatile solvent. Such varnishes are often very convenient, and are fairly good protective agents. For various reasons the amateur manufacture of such varnishes is not likely to be satisfactory, and it is, therefore, best purchased from a good maker.

One or two firms make a speciality of asphalt varnish, and with such the best results can be obtained. Unwilling as the author is to advertise any makers in this

connection, it is hardly possible to avoid so doing unless the valuable materials be passed over unnoticed. Of course, the exact composition and mode of preparation of such materials cannot be given, nor would it be much use to the engineer if they could, he is only concerned with the value of the material in use.

The first of these is an American preparation—Smith's durable metal coating. This dries with a beautifully smooth bright surface, and seems to have a very high protective power. The author has made some experiments with it, but the time over which such experiments can extend is so short that they are of little value compared with actual experience. It has been largely used for structures of all kinds in the United States with great success.

The other of these is the preparation so well known under the name "Bitumastic," which is made by Messrs. Wailes, Dove, and Company. It is made in two forms, one, which is applied only by the makers, having to be applied hot. This is called "bitumastic enamel," and the other, which can be applied exactly in the same way as an ordinary varnish, is called "bitumastic solution." These are both black, and dry with a bright smooth surface.

These are a perfect protection against rust under ordinary conditions. The material which forms the dried varnish is impervious to air and moisture, and at the same time is so elastic that it is not easily broken away. The author has made experiments with this material, and ranks it very highly as a protective agent,

and he has made many inquiries in places where it has been used, and the reports have been uniformly satisfactory.

These varnishes are, of course, black, though it would be possible, but probably not advantageous, to alter the colour by admixture of pigments. If, however, another colour is necessary, paint could be applied over the hard dry layer of black material, this being just covered with a coating of painter's "knotting."

TAR AND PITCH COATINGS.

Cast-iron water pipes and similar articles which have to be buried in the ground, and thus exposed to corrosive agents, and which have to be made at such a low price that any costly painting or other protection is out of the question, are usually covered with a layer of a tar or pitch composition of high melting point. The mixture is melted in a boiler, which must be sufficiently deep, and the pipe is lowered vertically into it. Sufficient adheres to make a good protective coating, which hardens as the pipe comes into the air and cools.

Very many compositions are used, each maker, no doubt, having his own modification, but the mixture suggested by the late Dr. Angus Smith answers very well, and is the basis from which most of the mixtures have been derived. It consists of a mixture of gas tar with thick oil from gas tar, the mixture being heated from 300 deg. to 350 deg. Fah.

Tar alone is sometimes used, but is not satisfactory, as it does not adhere well, and is often acid.

PREPARATION FOR PAINTING.

The preparation of the article for the paint and the actual painting are of quite as much importance as the character of the covering material used. What preparation can be given will depend on the nature of the article and on whether it can receive its final coat of paint, or whatever is to be used, in the shop or under cover, or whether the painting must be done outside in the open air. The latter is the more usual case, and will, therefore, be considered. The operations will, in general, be five in number:—

- (1) The preparation for a preliminary protective coating in the shop;
- (2) The application of such a coating;
- (3) The treatment of the metal from the time it leaves the shop till it is to be painted, such as removal from one place to another, etc.;
- (4) The preparation for the final painting;
- (5) The final painting.

Before any paint or other protective coating is applied the surfaces must be thoroughly cleaned, every trace of rust and scale being removed. This may be done either in the dry way by friction, or in the wet way by pickling, whichever is most convenient under the circumstances.

The cleaning in the dry way is usually done very inefficiently; indeed, it is safe to say that it cannot be done satisfactorily in the ordinary way with scrapers, chisels, wire brushes, or any other hand process, since these will only remove loose dirt, but will not touch firmly adherent scale, and that the only really efficient

method is the use of the sand blast. As is well known, this consists in the projection against the surface to be cleaned of sand or other hard finely-divided material under a considerable pressure of air, 20 lb. to 25 lb. per square inch being usually used. The sand must be perfectly dry, and after use it is sifted, the fine dust being rejected, and that which is sufficiently coarse being used over again. By this means perfect cleaning can be obtained, the metal showing its uniform grey colour.

When pickling is used, the pickling liquid is almost always dilute sulphuric acid (oil of vitriol), and containing from 20 to 25 per cent of acid. It is preferably used warm, and the articles are left in it till the surface is perfectly clean and free from rust and scale. The time taken may vary, according to the condition of the metal, from a few minutes up to an hour or so. Hydrogen is evolved, and this effectually loosens adherent scale, which falls off. A much weaker acid than that mentioned is sometimes used, or the acid is used cold, but in these cases the article must be cleaned with alkali so as to remove grease before it is put into the pickling vat. After pickling the acid must be removed from the surface as rapidly as possible, and this is best done by means of a jet of water discharged at a high pressure, mere rinsing not being efficient for the purpose. A jet at a pressure of from 100 lb. to 200 lb. is recommended by Prof. Sabin. Care also should be taken that the acid is pure, as if it contains arsenic, or certain other elements, some of these may be deposited on the metal. Hydrochloric acid (spirits of salts, muriatic acid) may be used

in place of the sulphuric acid, but is not so satisfactory. If the metal be allowed to dry in air the surface is likely to rust. To avoid this it should be put into a boiling bath of milk of lime, and left in this till it has acquired the temperature of the bath. It is then taken out, dried in an oven, and when dry the lime is brushed off. The surface left by pickling is specially susceptible to rust, and, therefore, a protecting layer of some kind must be applied at once.

The usual protecting layer is one of raw linseed oil, which is spread evenly over the work. This has the great advantage that it is transparent, and therefore allows the surface of the metal to be inspected, but it has the disadvantage that it takes a long time to dry, and that while drying it is soft and sticky, and, therefore, any dirt which comes in contact with it will adhere, and that when dried it is of little use as a protective agent; indeed, frequently it is injurious, as it hinders the adhesion of the paint which has to be subsequently applied, and this is specially likely to be the case if inferior oils are used, or still more if mineral or non-drying oils are used, as is sometimes the case.

A far better plan is to have the inspection made at once, and then a coat of paint or other protective can be applied within a few hours after the cleaning is complete, so that there will be little time for rusting. If paint be used it should be of the best quality, and must flow quite freely. It should not be diluted with volatile solvents, but with raw linseed oil. Any portions that are not to be painted should be rubbed over with a

good non-drying oil, which can afterwards be wiped off.

Some engineers contend that the best result would be obtained by dipping the article in a bath of hot paint at 175 deg. Fah., and leaving it there for 15 minutes or more, but this would obviously be impracticable in most cases.

The metal must be perfectly dry when the paint is applied, and preferably should be at a temperature slightly above that of the atmosphere, so as to prevent the possibility of the deposition of moisture on it. A higher temperature is of little advantage, except that it may make the paint flow better, unless some form of varnish paint is being used.

Until these operations are complete and the paint dry the metal must be kept under cover, protected from the weather. The separate portions must be supported on trestles, or otherwise clear of the ground, so that the air can have free circulation round them. Great care must be taken in all handling not to damage the surface of the paint, and if they have to travel the pieces must be well packed so that they do not rub.

The preparatory part of the work being thus done, the next step will probably be the bolting or otherwise fixing the various parts. As has been already pointed out, the access of air and moisture to the space between plates or into crevices is a prolific source of corrosion. To avoid this care must be taken that there is a good layer of paint on the surfaces that are to be in contact.

These are, therefore, cleaned and painted with a second coat before they are brought into contact.

Any crevices, cavities, etc., which will be inaccessible for painting when the structure is erected, must be filled up with some material which will be non-corrosive, and which will prevent access of air and moisture. Many substances may be used for this purpose, a hard asphalt paint or a tar or pitch mixture being good, but Prof. Sabin recommends a composition of litharge and glycerine made into a thick paste. This, he says, has no action on the iron even in presence of water, is quite insoluble and water-proof, and has considerable elasticity. He also recommends a mixture of three or four parts of hard asphalt with one part of linseed oil as being very satisfactory.

When the structure is erected it receives its final coat of paint of the character which has been selected, two or three coats being used, as the case may be. Owing to the contraction of the first formed skin, the paint is pressed away from edges and projecting points, so that these must receive a specially good coat, or the layer there will be thinner than on other parts. Great care must also be taken to clean thoroughly and re-paint any parts from which the paint has been rubbed off.

The outside painting must only be done in suitable weather—never when it is freezing, raining, or misty; indeed, it should only be done on days when the temperature is so considerably above the dew point that the deposition of moisture is unlikely. If the paint needs thinning, this is best done by heating the paint itself, rather than by the addition of thinning substance.

If these precautions or others of a similar character be

taken, the paint will have the best possible chance of standing well. If the engineer in charge of the work fully realises the importance of its preservation when once completed, and considers carefully the nature and cause of corrosion, he will have no difficulty in drawing up specifications and seeing that the work is done in the best possible way to ensure a durable structure. Each portion will, of course, require treatment suitable to its position in the whole and the requirements to which it will be subjected, but all parts must be efficiently protected from air and water.

With any form of protecting agent the same care is necessary as to the cleanliness and dryness of the surfaces.

Mr. H. L. Barker, of the Pennsylvania Railroad, in a paper read before the American Society for Testing Materials, in Atlantic City, on June 30th, 1905, suggested a novel method of protecting ironwork exposed to the air. He suggests that a layer of somewhat "tacky" paint be applied to the thoroughly cleaned surface, and that while this is wet a sheet of water-proof paraffined paper be pressed into close contact, the joints of the paper overlapping. On this other coats of paint are put as required. It is contended that the paper perfectly prevents the access of moisture to the metal, and therefore prevents corrosion. Time alone will show how far this can be depended on, but Mr. Barker's results, as far as his experiments have been published, are favourable. It is obvious that the process could only be applied to flat surfaces.

RE-PAINTING.

The question of re-painting structures of iron and steel is of very great importance. The first painting can only last a limited time, and it is essential for the permanence of the structure that the painting should be repeated at intervals, and that the re-painting should be as durable as the first painting. The conditions under which a structure has to be re-painted are usually such as to make good work far more difficult, and yet, if it be not well done, corrosion will go on at an ever-increasing rate.

The conditions which determine good painting are much the same in all cases. The surface to which the paint is to be applied must be quite clean; if possible, all the old paint should be removed, but if not, at least all that is not firmly adherent must be got rid of, and, of course, all rust must be removed. The cleaning may be done by scraping, or rubbing with stone or wire brush, or by other mechanical means of hand-cleaning, by the use of the sand blast, or by the use of solvents, a strong solution of caustic soda mixed to a paste with lime being the most general. Whichever method is adopted, the surface must be quite dry before the new paint is applied, and the right condition of dryness is often extremely difficult to get.

Of all the methods of cleaning, the sand blast is the most efficient, and should be used whenever possible. It must always be remembered that no painting, however good the materials and work may be, can possibly be durable if it is laid on a dirty surface.

OTHER METHODS OF PROTECTING IRON AND STEEL.

The other methods of protecting iron and steel call for little remark. Enamels similar to those used in the manufacture of pottery are largely used for the protection of small articles, especially those for domestic use, for notice boards of various kinds, and other similar purposes. The metal may either be coated with an opaque tin enamel, or first with a coating of an opaque pottery body, and then a transparent enamel above that, the latter method being the best. The methods of making enamelled ware have now reached a high degree of perfection, each maker having his own formula, which he usually keeps secret.

Enamels of this kind are a perfect protection whilst they last. They are, however, very brittle, and are, therefore, easily broken by careless treatment, as one can easily see by inspecting a few notice boards of this character. They will not stand vibration, and are apt to chip more or less by the expansion due to changes of temperature. For this reason it is doubtful whether such articles are specially suitable for domestic use.

Other methods have been frequently suggested, such as a wash of lime mortar or of Portland cement, and these may sometimes be useful for temporary purposes. Lime mortar is non-adherent, and is easily washed off, and is therefore of little use. Cement does not adhere very well, is more or less porous, and, being brittle, will not stand vibration, nor, unless the layer be very thick, is it of much value. Pieces of iron well coated with

cement and exposed to the weather showed distinct signs of rusting in two or three weeks, so that cement could not be depended on as being an efficient permanent protection, but pieces embedded in cement about half an inch thick all round showed no sign of rusting after many months' exposure.

In this connection important questions may arise as to the use of iron and steel in buildings. In modern steel-frame buildings the steel is so hidden that it is impossible to get at it for re-painting or examination. It is quite customary to use cast-iron columns and steel girders in structural work, these being completely cased in masonry, cement, or concrete, so that examination is impossible, and the life of the structure must depend largely on the durability of the metal itself. It may, of course, be said that the ironwork is so massive that even should corrosion go on it will not be sufficient to destroy the structure in any time during which it is likely to stand, but the rate of corrosion is so uncertain that such considerations can be little relied on.

The author has no definite data as to the durability of iron or steel under such conditions, so that the question can only be considered generally.

Stone and brick are porous, and absorb a considerable quantity of water, so that they would give little protection by themselves. Lime mortar absorbs water and carbon-dioxide so readily that it should effectually prevent corrosion, and soon becomes hard and almost impervious to water. The action of concrete containing lime would almost be the same. Portland cement



absorbs water so readily and hardens so quickly that, if thick enough, it should also be a good protective agent. There seems, therefore, to be little fear of the rapid corrosion of ironwork embedded in masonry. As a precaution, however, the following conditions should always be complied with: The column or girder should be completely cased in concrete or cement, leaving no portion of the iron covered by a layer less than, say, 1 inch in thickness, and, in case of hollow columns or other members, these should be filled with cement, so as to exclude moisture. If the columns or members were coated inside and out with a protective material preservation would be more certain.

The author will be very glad if any reader who has come across cases of corrosion of metal-work in buildings under such conditions will send him particulars.

CHAPTER III.

ATMOSPHERIC CORROSION OF OTHER METALS.

THE conditions which determine the atmospheric corrosion of the other metals used in structural work are much the same as those already considered, but all the metals likely to be used are much more durable than iron and steel, though they are all lacking in other valuable properties of these metals, and are much more costly.

LEAD.

Lead is probably the most durable of the ordinary metals as far as atmospheric corrosion is concerned. On exposure to air the surface of the metal loses its brightness, becomes dark-coloured and rough. It is slowly attacked by air, moisture, and carbon-dioxide, a white basic carbonate being produced, which may remain adherent to the metal or may be washed away by rain. The action is, however, so slow that lead roofing, centuries old, is often found in perfectly good condition, and lead for such purposes is not usually protected by paint or in any other way. Lead also stands well in the atmosphere of towns, the acid fumes present in the air having little action. It is very largely used for gutter pipes and other fittings which are exposed to the air.

ZINC.

Zinc is not very largely used for structural purposes, though it is sometimes used for roofing. It is crystalline, and lacking in strength. As will have been seen from

what has been said on the subject of galvanised iron, zinc resists ordinary atmospheric corrosion fairly well. The surface becomes dull and rough, and a small quantity of a white carbonate is formed, which may remain adherent or may be washed away by the rain. The action is, however, only superficial, and is very slow, the metal remaining good for many years.

Acid fumes are very destructive to zinc, so that it is unsuitable for use in the atmosphere of towns. The salts formed by the action of acids are soluble, and are, therefore, quite readily washed away. Zinc, being electro-positive to iron, copper, and most metals, should not be allowed to come in contact with any of them, and should always be secured by nails which have been well galvanised, or protected in some other way, so that the iron does not come in contact with the zinc.

COPPER.

This metal also resists atmospheric oxidation very well. The surface speedily darkens on exposure to the air, and it then becomes covered with a green deposit of a basic carbonate of copper, popularly, but wrongly, called verdigris. This carbonate is insoluble, and is usually adherent, so that it remains on the surface of the metal and protects it from further action. Copper is occasionally used for roofing, but is too costly for general use. It, however, stands well, and copper plates exist in good condition after centuries of exposure to the air. The acids likely to be present in the air of towns do not materially accelerate the decay of copper.

TIN.

The use of tin for the protection of iron has already been noted. It is not a durable metal, and is not used, except as tinplate, in structural work.

ALUMINIUM.

Aluminium, on exposure to the air, loses its polish, and the surface becomes dark-coloured and rough, with usually a slight increase in weight. No carbonate is formed, and moisture, air, and carbon-dioxide have little action on the pure metal.

NICKEL.

This metal is now frequently used for ornamental work; hence its resistance to atmospheric corrosion is a matter of some importance. It is not acted on by air or moisture, except that the surface loses its brightness, which can, however, be restored by polishing, as the metal is very hard. As a rule, where nickel is used it is electrolytically deposited on some other metal, and, as already remarked, the electro-deposited metal is very porous, and allows air and moisture to permeate, and thus the metal below may corrode. Nickel should, therefore, be deposited on copper or a copper alloy, and never on iron or steel if it is required to withstand the atmosphere.

ALLOYS.

Various alloys are used, the most durable being the bronzes, alloys of copper and tin. Many of these stand well, becoming coated with the green basic copper carbonate.

CHAPTER IV.

CORROSION OF METALS BY CORROSIVE GASES.

IN a sense, as will be seen from what has been said above, the atmosphere may be regarded, at least under some conditions, as being a corrosive gas; but in this section consideration will be given to a few cases in which metals may be exposed to gases of a more strongly corrosive character than ordinary air. Only those metals will be dealt with which are likely to be exposed under the conditions to be considered.

The most common case is the exposure of metals to the products of combustion of fuel, with a larger or smaller excess of air, and two conditions may be considered: (1) Tunnel gases in which the products of combustion are given out into more or less confined spaces, so that they are mixed with large excess of air, and act at the atmospheric temperature; and (2) boiler tubes and flues in which the products of combustion are in contact with the metals at a higher temperature and with a smaller excess of air.

The essential differences between the two cases are that in the former the quantity of air which may be considered as an inert gas is much larger, and, the

temperature being lower, water can readily condense on the exposed surfaces.

The fuels ordinarily used contain, of course, carbon and hydrogen, with smaller quantities of other constituents.

Taking as an example a coal having the composition—

Carbon	75'00
Hydrogen	4'00
Oxygen	12'45
Nitrogen.....	1'4
Sulphur	1'0
Chlorine.....	'15
Ash.....	6'00
	<hr/>
	100'00

For each pound of coal consumed, .36 lb. of water will be produced, and if all the sulphur be burnt to sulphur dioxide, .02 lb. of this gas will be produced, but apart of it will certainly be oxidised to sulphur trioxide, which in presence of moisture will form sulphuric acid. The result will be, therefore, the production of an atmosphere containing a large quantity of water, carbon dioxide, and sulphur dioxide, and a small quantity of sulphuric acid, and as the water condenses it will dissolve a considerable quantity of these substances, and will produce a strongly acid solution, which, therefore, may lead to corrosion. In addition, there may be considerable quantities of soot, which, by forming a porous hygroscopic mass, may retain the acid solution and thus facilitate corrosion.

The action of the small quantity of chlorine often

present in coal is very strongly marked. It is, no doubt, present in the coal as intermixed salt. On combustion this may be volatilised to some extent, but it is mainly decomposed, probably by the action of the silica present in the coal in conjunction with the moisture, silicate of soda being formed and hydrochloric acid being produced, which may have a very corrosive action, and which, being very soluble, will be carried down by the condensed water. As a rule, even when chlorine is present in the coal, none is found in the ash; so it is quite certain that it is volatilised. It has recently been pointed out that under some circumstances chlorine may be evolved, carbon dioxide and oxygen at a high temperature, as in flue gases, decomposing chlorides with the liberation of chlorine. The reaction for barium chloride is given as $\text{BaCl}_2 + \text{CO}_2 + \text{O} = \text{BaCO}_3 + 2\text{Cl}$. It was found that the action was least with sodium chloride and greatest with calcium chloride. In no case was more than a small proportion of the chloride decomposed, but even a very small quantity of such a corrosive gas as chlorine may have a distinct action in producing the corrosion of metals.

The author has no analyses of the air of railway tunnels or similar closed places in which the products of the combustion of fuel may accumulate, nor indeed would such analyses be of much value, as the most injurious constituents would be condensed, and thus would not appear in the analysis; but the general considerations as to the composition of the fuel and the products of combustion will show what must be the nature of the

gases. It will also be seen that such a gas must necessarily be powerfully corrosive, the corrosive agents being the same as those in the impure air of towns, but being present in much larger quantity.

Moisture and oxygen will play their part, as already explained, but the most active corrosive agents will be the sulphuric and hydrochloric acids which are necessarily present.

The following analyses of rust from iron in the tunnels of the underground section of the Caledonian Railway in Glasgow will at once indicate the nature of the corrosion which goes on, and it will be seen that both sulphates and chlorides are present in considerable quantity, thus showing that both sulphuric and hydrochloric acids have been at work.

Analyses of Iron Rust from Glasgow Tunnels.

	1	2	3	4
Ferric oxide	59·86	66·70	63·90	66·65
Ferrous oxide	1·64	1·64	2·01	1·26
Ferrous sulphide	1·33	0·33	0·86	1·04
Sulphuric acid (SO ₃).....	9·00	5·05	5·75	5·49
Chlorine	2·09	2·02	0·40	0·60
Insoluble (non-volatile) ...	7·14	4·84	0·70	6·55
Moisture and organic matter	18·94	19·42	26·38	18·41
	100·00	100·00	100·00	100·00

The protection of ironwork under such conditions is almost impossible. A good asphalt varnish will probably stand longer than any other protective coating, but this must go in time, and its renewal being, under

the conditions of damp and dirt, almost impossible, corrosion will necessarily continue till the ironwork is destroyed.

The use of iron or steel under such circumstances is, therefore, not advisable, and all tunnels in which coal or coke-fired engines are used should be built of good brick.

If metal be used, as, unfortunately, it very often is, it must be subject to constant and most careful scrutiny, or disaster may follow, and, in any case, frequent costly renewals will be necessary.

BOILER TUBES, ETC.

The only other conditions under which metals are used, where they are subject to the action of products of combustion, are for firebox plates and boiler tubes. In these cases the metal has water on one side, and the gas containing the products of combustion on the other, so that the temperature can never be very high, but will always be above the boiling point of water—at least, when the boiler is at work—so that there will be little chance of the deposition of moisture, and the conditions are quite different to those under which atmospheric corrosion takes place. In such case, corrosion may take place either from the water side or the flame side. The latter case alone will be considered here; the former will be dealt with later, when the action of water on metals is considered.

The only metals that need even brief consideration in this connection are iron and steel, used both for firebox

plates and boiler tubes; copper, which is used only for firebox plates; and brass, which is only used for boiler tubes.

IRON AND STEEL.

Malleable iron and mild steel are now largely used for firebox plates and tubes, and their use is rapidly growing, and, considered only from the standpoint of the action of flue gases, they must be regarded as being very durable. Unfortunately, as will be seen later, they are much more readily corroded from the water side, and, therefore, whilst they stand well under some conditions, they are rapidly destroyed under others.

Direct oxidation can only play a very small part in the corrosion of iron or steel under the conditions being considered, for the temperature is not high enough for oxygen to attack the iron at all rapidly, and ordinary rusting is not likely to go on, because the temperature is too high to allow of the deposition of moisture, which, as has been pointed out, is essential to rusting. The atmosphere, too, will often be very strongly reducing owing to the partially-burnt gas and tarry matters which are swept into the tube. In the case of firebox plates, air may find its way in at the edge of the fire, and, therefore, reach the surface of the vertical plates, which, owing to their thickness, will be at a moderately high temperature, and direct oxidation may thus take place, the plate being slowly oxidised away.

In iron and steel tubes the rusting may be set up by the deposition of moisture in the cold tube when the

fires are first lighted, but under ordinary circumstances this will not do much harm, as the temperature will soon rise high enough to dry the rust, and thus stop further action, though as cooling again takes place the spot of rust may form a nucleus at which corrosion may start, but very often such oxide may be reduced by the reducing gases or deposited carbon from the fuel. If the boiler be standing unused for any length of time, rusting may go on rapidly owing to the deposition of moisture, and any leakage of water may, of course, set up rapid corrosion.

The following analyses of deposit from two locomotive boiler tubes will illustrate the possible internal corrosion of such tubes. The deposits were quite black and light and looked like coke, and they were firmly adherent to the surface of the tube:...

	1		2
Ferric oxide.....	2·80	2·05
Alumina	1·85	1·85
Insoluble matter.....	2·25	2·80
Chlorine	·12	·21
Sulphur*	2·75	3·20
Carbonaceous matter	80·53	77·69
Moisture	5·55	6·10
Not estimated	4·15	6·1
	<hr/>		<hr/>
	100·00		100·00

No. 1 was an iron tube which had been in use nearly six years, and No. 2 was a steel tube which had been in

* Only a small proportion of the sulphur was present as sulphuric acid.

use four and a half years. No. 1 showed considerable corrosion both inside and outside, whilst No. 2 was much less corroded inside.

As will be seen from the analysis, the deposit is almost entirely derived from the fuel, consisting as it does largely of carbon and carbonaceous matter from the smoke, and silica and alumina from the coal ash. What corrosion has taken place is obviously due to the action of sulphuric acid, probably taking place mainly when the tube was cooling or cold.

Iron and steel resist the action of flue gases at a moderate temperature fairly well. At high temperatures, however, oxidation is very rapid. When iron or steel boiler tubes fail it is almost always mainly on account of corrosion from the water side. No protection that could be applied inside the tube would have any effect in lengthening its life.

BRASS.

Brass tubes are largely used for boilers, and are general for locomotive work, though of late iron and steel tubes have been finding considerable favour, partly because they are much cheaper, and partly because with the very long boilers now in use great rigidity is necessary, and the iron and steel tubes are much more rigid than those of brass.

For boiler tubes the brass almost invariably contains 70 per cent of copper and 30 per cent of zinc, though in certain cases, alloys, either richer or poorer in copper, are used. Experience has shown that for boiler purposes

this composition is the most suitable, and it is sufficiently ductile to allow of the tube being readily drawn. Solid-drawn tubes are always used—never brazed tubes.

The structure of brass will be discussed later. Suffice it to say in this connection that brass of this composition is homogeneous, crystallises as a whole, and may be regarded as being a solution of zinc in copper.

Brass is very much more readily acted on by flue gases than is iron or steel; hence brass boiler tubes corrode much more rapidly on the inside; but as the metal is hardly acted on by water, little corrosion takes place from the water side, and the tubes are on the whole much more durable than those of iron or steel.

Brass tubes almost invariably fail by corrosion from the inside, the corrosion being irregular, and ultimately forming holes through the tubes. Very frequently the tubes fail near the firebox end, where, of course, the gases are hottest, and where the hot flame may play directly on the metal, and where very hot solid material may be projected against it. The draught in a running locomotive is very powerful, and the effect of projected solid matter from the fuel cannot be entirely neglected. It must be remembered that in a boiler tube, under ordinary conditions, the flame does not come in contact with the metal, there being a cold zone of no combustion, due to the cooling action of the water; but where the flame is directed against the metal with any force this is not the case, and even though the metal is a very good conductor of heat, it may become very hot locally.

Copper is only slowly acted on by dilute sulphuric

acid, but would probably be readily attacked by the acid in the condition in which it occurs in flue gases; nor is it attacked readily by hydrochloric acid in solution, but the gaseous hydrochloric acid and still more gaseous chlorine attack it readily. Zinc is readily attacked by all acids. The result is that both zinc and copper are attacked, sulphates and chlorides being formed. Chlorine in some form is the most active corroding agent.

A sample of the deposit from the inside of a corroded boiler tube (70/30) was found to contain—

Copper	40·81
Chlorine	22·35
Sulphuric acid (SO_3).....	6·90 (S2·76)

with only small quantities of carbonaceous matter and coal ash. The interior of the tube was rough and irregularly corroded, and in one place the corrosion had gone through, forming a hole.

It is quite obvious that not only is chlorine in some form the principal corroding agent, but that, unlike the case of the iron tube previously mentioned, a large proportion of the deposit is derived from the tube itself.

The chlorine, as already remarked, may be present in the gas as hydrochloric acid, and to a smaller extent as free chlorine, and under ordinary circumstances it can only be derived from the coal. In the case of marine boilers leakage of sea water may account for some chlorine, but in ordinary land boilers the water contains so little chlorine that a leakage could have little action.

The quality of the brass—that is, the amount of foreign

metals present in small quantity—seems to have no influence on the resistance of the metal to corrosion.

There are few more puzzling phenomena than the irregular corrosion of boiler tubes, and in most cases it is impossible to decide why it has taken place in one way rather than another, and why the tube should be specially acted on in one spot so as to form a hole. The author believes that the irregularity is due to what can only be called accidental causes, such as the deposition of a little soot, which serves as a nucleus for the condensation of acid, or perhaps some portions being protected by a tarry deposit from which other portions are free, or from the many other minor circumstances that may retard or accelerate corrosion. He believes that in general the durability of a tube depends very largely on the amount of chlorine in the coal, which, as before remarked, is very variable. Coals from some districts contain a considerable amount of salt, whilst those from others are nearly or quite free. Copper is quite as readily acted on as zinc under the conditions which exist in an ordinary boiler tube, so that, even could copper be substituted for brass, its tubes would be not more, but probably less durable.

COPPER.

Copper is largely used for firebox plates, for which it has many advantages. The plates are, however, thick, so that the inside may become heated to a fairly high temperature, and also the flame may impinge upon the surface with considerable force. The copper is to some extent

oxidised, and also is attacked by the chlorine exactly as in the case of brass boiler tubes. A very pure metal does not seem to be any advantage, the impurities usually present having little or no influence in hastening corrosion. In many, perhaps most, cases the failure of boiler tubes and firebox plates is not due to what may be fairly called corrosion, but rather to mechanical causes. No protective covering can be applied.

LEAD.

Lead is sometimes used for pipes and other apparatus where acid gases are to be dealt with, and of all the metals it is least liable to corrosion by such substances. Its use for the manufacture of the lead chambers, for sulphuric acid making, which have to come in contact with hot air, steam, sulphurous and sulphuric acids, and oxide of nitrogen, is well known. A minute trace of zinc seems to increase the liability of the lead to corrosion, and lead which is to be used for acid chambers and similar purposes is always de-silverised by the Pattinson --never by the zinc--process.

CHAPTER V.

CORROSION OF METALS BY WATER AND OTHER LIQUIDS.

THE only corrosive liquid that need be considered in ordinary cases is water, not, of course, pure water, which would probably have very little action on any of the metals, but water in the more or less impure form in which it is met with in nature. Excluding the various mineral waters, all natural waters may be classified into fresh water and salt water. The former will include all ordinary stream or spring water, even though considerably contaminated with foreign matter, whilst the latter consists of sea water, which varies only slightly in composition.

In general, metals may be exposed to the corrosive action of water of either kind under two sets of temperature conditions, and these may very considerably modify the corrosive action:—

- (1) Cold—*i.e.*, at ordinary atmospheric temperature;
- (2) Hot.

CORROSION OF IRON WATER PIPES.

The most important example of corrosion in the cold is in that of pipes used for the conveyance of water, and the metals of importance are iron or steel and lead, pipes

of other metals only being used to a very small extent. The pipes are frequently embedded in the ground, and are, therefore, exposed to corrosion both inside and outside; inside from the water which they have to carry, and outside from the water which percolates into the earth and becomes contaminated with various substances which may greatly increase the rate of corrosion. Of exactly the same character as this external corrosion is that by which other iron or steel articles covered with soil are destroyed.

CORROSION OF IRON PIPES BY WATER.

Considering first the internal corrosion of iron or steel pipes carrying water, the water will usually be fairly pure, though it may contain calcium and other salts, but never in large enough quantity to impart a distinctive taste; and, of course, as is always the case with natural waters, it will always contain oxygen and carbon dioxide in solution.

Natural water under these conditions has a very powerful rusting action on the iron. The carbonic acid attacks the iron, forming a carbonate which, by the oxidising action of the oxygen in solution, is rapidly converted into an insoluble hydrate or rust, the action being exactly the same as that which takes place when iron is exposed to the air, only that in the case of a pipe carrying water it can go on continuously, as a fresh supply of the necessary corroding agents will always be at hand. A pipe will probably not rust more when the the water is still than when it is flowing, but rather the

reverse, though it is often thought that such is the case, because when the water is started to run from a water pipe the contents of which have been at rest for some time, a considerable amount of rust is brought away.

The action of water on iron of all kinds is very marked. If a piece of iron be immersed in water, rusting begins very rapidly, and in a few days a copious deposit of rust will be obtained; and this is in most cases due to direct chemical action. Electrolysis may take a small part in the action, but it can only be a very small part, and then must be due to the presence of impurities, for pure water does act as an electrolyte.

The character of the internal corrosion of a water pipe can largely be judged as in other cases by the nature of the deposit formed, which must necessarily be derived from the water and the pipe, together with any solid matter that may have been deposited from the water. Such a deposit will, therefore, consist mainly of ferric hydrate, as in ordinary rust, mingled, perhaps, with graphite from the iron, if cast-iron pipes have been used, together with some mineral matter and probably a considerable quantity of organic matter. This last having been entangled in the rust and thus retained, will probably include a fair proportion of living organisms which can flourish under such conditions, and these may possibly increase the rate of corrosion.

Very little has been published on the question of corrosion of water pipes, and very few analyses of the deposit are available. Mr. Mansergh, in a paper read before the Institution of Civil Engineers, in 1882, on

the Lancaster Waterworks extension,* gives an analysis of a deposit scraped from tubes which had been in use some years as being—

Iron protoxide	7
Silica in minute crystals (silver sand)	2
Alumina	2
Lime, other soil matters, and loss.....	2
Organic matter and water of composition.....	23
Water	64
	—
	100

This analysis, it will be seen, is so imperfect as to be of little use. The iron, for instance, will certainly be present as peroxide, not as protoxide, and there is no mention of sulphates, which are probably always present, soluble sulphates in solution taking an active part in the corrosion. As the current of water in pipes is usually not very rapid, a large amount of deposit may accumulate sometimes; nearly blocking the pipe.

The outside of the pipe is subject to very different conditions. It will almost always be wet, though it may sometimes be comparatively dry, and therefore may be exposed to the air. The water which comes in contact with it will probably be charged with mineral salts, and also with various organic matters from the soil through which the water has passed, and these may be acid and may have a very considerable effect on the corrosion. The conditions, therefore, are specially favourable to corrosion, since it may be taken as a general rule that

* Minutes of Proceedings, vol. lxviii., page 259.

the presence of any electrolyte—*i.e.*, salt decomposable by an electric current—in solution will tend to produce corrosion.

Pipes are very rarely laid “bare,” and if they are corrosion will take place very rapidly, but they are usually protected by a layer of some preservative, Dr. Angus Smith’s composition being usually used for cast-iron pipes, as it is cheap and fairly durable. The mixture is used hot, and of such consistency that a uniform layer is formed over the metal. Pipes so coated may last for years with but little corrosion. Indeed, water pipes are cast so thick that the first sign of corrosion is usually not the failure of the metal, but the diminished flow of water owing to the pipe becoming blocked by the development of a deposit inside, which always has much greater bulk than the iron removed. Galvanising seems to be of little use under these conditions, the zinc being rapidly dissolved, and zinc does not seem to exercise any great protective action except as a covering, for it will be found that iron in contact with zinc rusts as rapidly under the influence of water as iron alone, except in the immediate neighbourhood of the zinc, this seeming to show that the action is mainly due to direct oxidation, and that there is very little electrolytic action.

For the outside of iron pipes, and, indeed, of all iron articles or structures that have to be exposed to wet soil, a layer of asphalt varnish is probably the best protective agent, and a thick coating of Portland cement concrete is almost impervious to water, and therefore

will tend to prevent corrosion. It will, however, add to the difficulty of removing the pipes, should a removal be necessary.

Under the conditions to which pipes are exposed, cast iron seems to stand better than wrought iron or mild steel.

CORROSION OF LEAD PIPES.

Next in importance and interest to iron or steel for pipe purposes is lead, which is almost universally used for house water pipes and other connections. As, therefore, drinking water is generally supplied through lead pipes, and as lead in solution is highly poisonous, the question of the action of water on the metal is one of great importance.

It is well known that lead is not acted on by pure air-free water, but that water containing oxygen slowly attacks it, a hydrate being formed which is slightly soluble in water, and is therefore dissolved (1 part of the oxide dissolves in about 7,000 parts of water), and if carbon dioxide is present, as, of course, is always the case in natural waters, the oxide will be converted into carbonate.

The action of water on lead is very materially influenced by the presence of salts in solution, even very small quantities, little more than traces in some cases, having a very decided influence, the action being accelerated by some salts and retarded by others, sulphates, chlorides, and phosphates having the most marked retarding action, whilst ammonium salts, especially the nitrates,

seem to accelerate corrosion. As the salts most usually present in natural waters are chlorides and sulphates, it will be seen that natural waters will, as a rule, have less action on lead than pure water, and, within limits, the less pure the water the less will be its corrosive action. The variation is very probably due to the varying solubility of the basic carbonate PbCO_3 , Pb(OH)_2 in solutions containing various salts.

Carbon dioxide seems to play but small part in the corrosion of lead, since water saturated with carbonic acid has but little action, though its solvent action is considerably increased under pressure. The solubility of lead is very greatly increased by the presence of even traces of free acid, and as some natural waters are distinctly acid, these may dissolve appreciable quantities of lead, and in many cases where a town water supply has actively corroded lead pipes, this has been found to be due to the presence of traces of acid.

The whole question of the action of water on lead is of very great importance, and though the questions that arise cannot be said to have been all settled, very much has been ascertained, and the character of the water that has the most vigorous action is now known. The action is greatest in a water well aerated and free from mineral matters—that is, of a high degree of purity—such water, in fact, as is drawn from upland collecting grounds or from lakes in hard, insoluble rocks; whilst it is least in the case of less pure waters derived from rivers and springs which flow over or through the softer and more soluble rocks.

Prof. P. F. Frankland* some years ago made a series of experiments on the influence of a very soft water on lead pipes. He found that lead was attacked, but that the amount dissolved reached a maximum in one day, and did not increase on longer exposure. He found, also, that agitation with carbonate of lime, or addition of a little carbonate of soda or lime, prevented all action on the lead.

Messrs. Crookes, Odling, and Tidy, dealing with the water of Huddersfield, found that the corrosive power was greatly reduced by filtration through sand, carbonate of lime, and flint, and they attributed this to the solution of a small quantity of silica. Prof. Frankland repeated the experiments, and obtained similar results, and he found that water filtered through flint actually took up about 15 parts of silica in 100,000.

The action which water will have on lead, however, cannot always be judged from its chemical composition.

Commercial lead is usually very pure, and the addition of foreign constituents in practicable proportions seems to have little influence on its corrodibility, though a small quantity of tin is often added to harden the metal.

When lead pipe is acted on by water, the corrosion is always more or less irregular, some portions being hardly attacked, whilst at other places holes may be eaten through. This does not seem to be due to any irregularity in the metal, but rather to merely accidental circumstances. A white deposit is always formed inside

* J.S.C.I., 8 (1889), page 243.

the pipe, which consists mainly of basic carbonate with some sulphate.

Attempts that have been made to protect lead tubes from corrosion by an internal coating of tin or other metal do not seem to have been very successful.

CORROSION OF BOILERS.

The corrosion of steam boilers is a matter of such vital importance to the engineer that it is surprising that there is such a small amount of literature on the subject. A few papers have been written and published in the journals of the various societies, but these deal mainly with special aspects of the case, and no exhaustive study of the subject seems to have been made. This may be due to the practical difficulties of such a research, but it is none the less disappointing. As a result there are many points which are still obscure, and all that can be done is to point out in a general way the nature of the corrosion and the reactions by which it is usually brought about. Everyone who has had any experience with steam boilers will know how uncertain and erratic the phenomena of corrosion seem to be, and how difficult it is to reduce them to any rule. This is probably largely due to the fact that in a steam boiler, under ordinary circumstances, the conditions are just on the borderland between stability and instability, and that therefore a seemingly unimportant change in the conditions may lead to considerable variation in the result.

In an ordinary steam boiler there are three forms of corrosion which have to be considered:—

- (1) External corrosion (α , on parts exposed to air;
 β , on parts exposed to products of combustion);
- (2) Internal corrosion whilst the boiler is out of use;
- (3) Internal corrosion whilst under steam.

(1) Of external corrosion of parts exposed to air nothing need be said, and on that of parts exposed to the gases but little, for in this case the conditions are exactly the same as those already discussed in the case of boiler tubes. The products of combustion, consisting of carbon dioxide, steam, and excess of air, with small quantities of other gases, come in contact with the boiler at such a low temperature that there is very little action under ordinary conditions. If, however, the temperature of the boiler plates becomes unduly high—as may happen, for instance, if there is a deposit of scale inside—it may become high enough for oxidation to go on, the plates being rapidly destroyed. When the fires are first put on a cold boiler, water from the products of combustion may condense on the plates and thus lead to the commencement of corrosion. External corrosion, however, is, as a rule, of little importance.

(2) When a boiler is out of use it will contain more or less water and moist air, and therefore will be in just the condition under which rusting can go on rapidly, and not infrequently the rusting, once started, may continue under other conditions which in themselves seem little suited to set up the action.

(3) When the boiler is under steam the conditions will be very different. It will contain water at above 100

deg. Cen., the exact temperature depending on the pressure of the steam, and the steam space will be full of steam mixed with small quantities of air and other gases; and these conditions would seem to be specially unfavourable to the setting up of corrosion. Yet not only does corrosion frequently take place, but it is very erratic in its character, and it seems impossible to foretell whether it will take place or not.

It is quite certain that, in most cases, the corrosion is not due to any peculiarity in the metal used for the boilers. It very frequently happens that of two boilers made from exactly the same metal and under the same conditions one will corrode and the other will not. It is not meant to assert that boiler plate is never under any circumstances defective, but only that the defects are not of a character to set up corrosion, and therefore that in a case of corrosion the cause need not be looked for in the metal.

The question of the relative liability to corrosion of iron and steel is one which need not be discussed here. Whatever difference there may be is not very great, certainly not great enough to lead to the selection of one of the metals rather than the other for boiler making.

The quality of the water used is of very great importance. Water used for boilers is never pure, but may vary from the comparatively pure water, such as that of Loch Katrine, to impure river water and sea water, or other water containing a large amount of salts of various kinds in solution. There can be no doubt whatever that impure water, especially such as contains acids or acid

salts in solution, will lead to corrosion, but it is only in few cases that this can be regarded as being the real cause, because even with pure water corrosion may take place.

Pure water has no action whatever on iron at any temperature likely to be met with in a steam boiler. It has been stated that it attacks the iron, forming a thin layer of black oxide, which acts as a protective agent. This, however, does not seem to be the case, though undoubtedly such an action does take place at a somewhat higher temperature. But the water as supplied to a steam boiler is not and never can be pure. It, being a natural water, always contains oxygen and carbon dioxide in solution, and these, it has been pointed out, are the active agents of ordinary rusting. When water containing oxygen or other gases is heated to boiling, these gases are expelled, but the expulsion is never instantaneous; indeed, the real cause of their removal seems to be that they are liberated from solution and are swept out by the escaping steam. In a steam boiler the water is being gradually converted into steam, and this will tend to sweep out the dissolved gases. The action will be rendered slower by the pressure in the boiler; but the gas would soon be expelled in the ordinary course. Whilst, however, there is air and carbon dioxide in solution rusting may go on very rapidly, for the high temperature of the boiler will tend to greatly accelerate the action.

The gas, as it is given out from the solution, will not be given out by any means uniformly, but will separate

in the form of bubbles on the surface in contact with which the solution may happen to be. This collection of bubbles on the surface being heated may be observed in any case where a solution of a gas is heated, and the slightest irregularity may be sufficient to determine the position of the evolution of the bubbles. If water be heated to boiling in an apparently quite smooth porcelain basin, the bubbles of gas will often be seen to be given off in a continuous stream from certain spots and not uniformly from all over the basin. Exactly the same thing happens in a steam boiler. There is an evolution of gas from the heating surfaces in the form of small bubbles which collect at certain spots.

If the gas be oxygen it seems at the moment of liberation to have active properties somewhat analogous to what is commonly called the nascent condition, and to be capable of attacking iron with the formation of oxide. Any little irregularity seems to determine the evolution of the gas. Thus the bubbles will be formed copiously round a rivet head or other similar projection, and the roughness left by the formation and removal of a little speck of oxide will be quite sufficient to determine a further evolution of gas, and therefore further oxidation.

There is no doubt that, in ordinary cases, pitting, which is so common in boilers, is due to this evolution of gas. The scale falls away, or is removed in solution by the carbonic acid in the water, and further oxidation going on at the same spot, the pit will be gradually deepened. It should be noted that pitting always takes

place on surfaces which are subject to direct heating, and never on other parts of the boiler.

If this be the cause of pitting, its prevention should not be very difficult. Gas can only be given off from water freshly supplied to the boiler, because the gas in solution will be quickly expelled, and therefore the action must be due to the feed water, which will always be saturated with air, unless it has been passed through a feed-water heater, by which the air will largely have been expelled, and the corrosion thus transferred from the boiler to the heater. The action can very often be modified by so supplying the feed water that it does not come in contact with the heating surfaces till its gases have been expelled. The action of oxygen on iron, when it is being given out from solution, seems to have been first noticed by Mr. J. Weir about 1872.* Mr. Weir contended that all corrosion of boilers was due to this evolution of oxygen from solution in what he called the nascent condition. He said, however, that the oxidation by itself was always superficial, but that the oxide was dissolved away by the carbonic acid in solution which dissolves out the oxide of iron as carbonate. He says: "First, when the feed water contains only the constituents of atmospheric air (oxygen and nitrogen) a coating of iron oxide is formed, and if this is allowed to remain there will be no further action; second, when the feed contains in addition carbonic acid in solution, the oxygen combines with the iron to form oxide of iron, which is acted on by the carbonic acid and changed

into ferrous carbonate. This is dissolved in the water and reduced by the oxygen in it to iron oxide, while the carbonic acid is liberated and is free to attack more iron oxide, and so on. All that is thus necessary to keep up the corrosion is a supply of oxygen in the feed water, as the amount of carbonic acid remains constant.”†

If this be the correct explanation of the phenomena, it is obvious that remedies are easy: (1) to remove the oxygen from the feed water by means of feed heaters or otherwise; and (2) to remove the carbonic acid by addition of lime or some alkali which will convert it into a stable salt.

There are, no doubt, other causes which may set up corrosion, due to the introduction of foreign matters into the boiler.

The presence of animal or vegetable fats brought over from the cylinders or other machinery is sometimes undoubtedly a cause of corrosion, though perhaps not so frequently to-day, as its influence is well known, and precautions are taken to prevent it. Fats which are salts of glycerine with a fatty acid are decomposed by water or steam at high temperatures, the fatty acid being liberated. This will float on the surface of the water, but will readily adhere to any surface with which it comes in contact, and corrosion will be at once set up. In an analysis of deposit from the pits in a badly-corroded boiler given by Mr. Couper*

* Transactions of Institution of Engineers and Shipbuilders. Vol xl., page 78.

† Transactions of I. of E. S. of S. Vol. xl., page 79 * Ibid., page 52.

no less than 2.45 per cent of fatty acids and 3.61 per cent of other organic matter was found.

Salts in solution in the water may have considerable influence. Most salts are probably without direct action, but any which can give off acid at the temperature of the boiler may have considerable effect. It has been pointed out, for instance, that some salts, such as magnesium chloride, which is always present in sea-water, dissociate readily with the liberation of hydrochloric acid, which would act rapidly on the iron. Against the theory that this action produces corrosion it has been urged that no ferric chloride has been detected in solution in the water, but in presence of a large excess of water and dissolved oxygen this would probably be decomposed with the precipitation of ferric hydrate.

The substances which are present in largest quantity in ordinary water, calcium carbonate and calcium sulphate, and which are so troublesome as scale formers, have little or no direct corrosive action. Their indirect action, however, may be very considerable from the formation of scale, and therefore the overheating of the plates. Such a deposit is, however, a protection against direct corrosion—at least until it becomes too thick.

So far only direct chemical action has been discussed, and no mention has been made of galvanic action, which is sometimes said to play such an important part in this and other forms of corrosion. That galvanic action may not take some little part in boiler corrosion it would

be too much to say, but its action is on a small scale, and is quite subordinate to direct chemical action.

In order that galvanic action may be set up, there must be two substances, which by their contact set up a difference of potential, so that a current flows and the electro-positive metal is dissolved away.

In the case of the ordinary steam boiler there is no such contact of substances under ordinary conditions, and where the boilers are fitted with brass tubes these are connected at both ends, so as to form a complete circuit. This does not seem to have any effect in promoting corrosion. Of course, if a fragment of copper or any electro-negative metal found its way into the boiler and came in contact with the iron, it would set up a local circuit which might lead to the formation of a pit. It has been suggested that copper salts might be brought in in solution from the copper or brass steam pipes, owing to the action of oils or other substances, and that these then might be decomposed by the iron, and the deposited copper might set up electrolytic action. This is no doubt a possibility, but it does not seem ever to have been proved to have been the cause of actual corrosion. It has also been suggested that the iron scale which is left adherent to the plates may set up such an action leading to the solution of the iron, but this again has not been proved to be an actual cause of corrosion.

In ordinary fresh water any galvanic or electrolytic action is extremely unlikely. The quantity of salts present is extremely small, and these are not of the

character to lead to such action; but in sea water, where the quantity of dissolved salts is much larger, under suitable conditions galvanic action might be set up. The conditions in an ordinary steam boiler, however, do not seem to be such as to favour electrolytic action in any case.

Under the idea that the action which led to the corrosion of steam boilers was electrolytic, it has been suggested to fix inside the boiler, and in good metallic connection with it, plates of zinc, so that the zinc, being the more electro-positive metal, might be dissolved away, and thus the iron protected. There seems to be a large amount of evidence to the effect that zinc does protect the iron and to some extent at least prevent corrosion. This is what is to be expected, for if the water contains any electrolytes (salts capable of decomposition) a current will be set up and the zinc will be dissolved, but even if the water contains no such salts the zinc will still be dissolved, for either fresh or sea water containing air in solution rapidly attacks zinc—in the cold apparently by direct oxidation due to the oxygen in solution, but at higher temperatures with evolution of hydrogen by the decomposition of water; and in either case the zinc salts formed will be converted by the carbonic acid present into carbonate, which will be precipitated. The solution of the zinc is, therefore, no evidence that there has been any electrolytic action, since it may be due to purely chemical causes, but as during solution it will remove the carbonic acid, and probably also the oxygen, both of which have such a deleterious effect on iron, it may thus

indirectly prevent corrosion. Stromeyer states that zinc salts in solution appear to reduce the corrosion of boilers, and if this be so it is a further explanation of the influence of zinc, and he suggests the painting of the inside of boilers with zinc oxide, or some other zinc salt (not the chloride). He says also that tin salts seem to increase the corrosion.

In certain cases the galvanising of the outside of steel boiler tubes has been found to considerably increase their life, and one important railway company is fitting its new engines with galvanised steel tubes.

As methods for the prevention of corrosion in boilers Mr. Stromeyer* gives the following:—

- (1) Substitution of mineral lubricants for animal or vegetable oils;
- (2) The use of fresh or even distilled water wherever obtainable in place of sea water;
- (3) The removal of air from feed water;
- (4) The use of zinc;
- (5) The use of alkalies.

He also states that in his opinion “the existence of galvanic currents in boilers has not been proved.”

* “Marine Boiler Management,” page 47.

CHAPTER VI.

CORROSION OF IRON AND STEEL BY SEA WATER.

THE action of sea water on metals is in many respects different to the action of fresh water, for sea water is a strongly saline solution, and the salts present may have an important action on metals.

The amount of salts in solution varies somewhat in different parts of the ocean, but may be taken as averaging, for the open sea, about 34·4 grammes per litre, or roughly, about 3·5 per cent. It is least in such seas as the Baltic—where it amounts to from 5 to 18 grammes per litre—in which there is a large supply of fresh water, and is greatest in such seas as the Dead Sea, where the supply of water falls short of the loss by evaporation.

There is but little variation in the composition of the salts in the open sea, and the following analysis by the late Prof. Dittmar, which is an average of 77 analyses of sea water, may be taken as fairly representing the salts ordinarily present:—

Chlorine.....	55·292
Bromine.....	·1884
Sulphuric acid (SO^3)	6·410
Carbonic acid (CO^2).....	·152
Lime (CaO)	1·676
Magnesia (Mg.O)	6·209
Potash (K^2O).....	1·332
Soda (Na^2O)	41·234
Basic oxygen, equivalent to the halogens—	12·493

It will be seen from these figures that, as is well known, the salt present in largest quantity is common salt (sodium chloride), which amounts to about 77·83 per cent of the total solids, or 2·68 per cent of the water, whilst there are other chlorides and some sulphates also present.

Sea water also contains gases in solution, to the amount of from 2·2 to 2·5 volumes in 100 volumes of water, made up according to Hunter, in one case, of—

Carbon dioxide	28·62
Oxygen.....	49·44
Nitrogen	21·94

this being very nearly the quantity and the proportions which are present in fresh water.

Dittmar comes to the conclusion that the presence of free carbonic acid in sea water is exceptional, the quantity found being less than that required to form bicarbonate with the bases present; the bicarbonates of the alkalies are stable salts, but the bicarbonates of the alkaline earths are much less stable, and if present they may act as if the carbonic acid were free. At the surface, where the water is in contact with the air, and near the shore, where it is receiving supplies of fresh water, the quantity of carbon-dioxide may be larger.

These considerations make the explanation of the action of sea water on iron and steel easy to understand.

The action which may take place may be of three kinds:—

- (1) Direct chemical action, due to the matters in solution, either solids or gases;
- (2) Electrolytic action, due to the setting up of local electric currents;
- (3) Action due to the influence of living organisms in the water.

It will probably be simplest to follow the order which has been adopted in previous chapters, and deal with the metals in series, since the action varies much in different cases, and it may be possible subsequently to summarise the reactions.

IRON AND STEEL.

All forms of iron and steel rust very rapidly in sea water, the action beginning almost at once, a mass of red rust being formed, and the action not being distinguishable as far as the eye can detect from the action in the case of fresh water. Nor does the rust differ in composition from that so formed, and the loss of weight in salt water is not very different from the loss of weight in fresh water under the same conditions. Lime in excess seems to retard the action, and if the water be boiled, so as to expel air and carbon dioxide, no rusting takes place, and no iron passes into solution, or, at anyrate, only the merest trace.

It is, therefore, safe to assume that under ordinary conditions rusting takes place in sea water exactly as it does in fresh water, the oxygen and carbon dioxide being the active agents.

When an iron article is immersed in sea water it rapidly becomes covered with rust, but the rust is only loosely adherent, so that if there is any friction, as by the movement of running water, it is rapidly worn away. The iron thus loses in weight by the rusting, but may remain free from visible rust. Under ordinary conditions, the rusting is not by any means uniform, but takes place mainly in spots, leading to pitting, exactly as in the case of fresh-water rusting. What determines the points at which the rusting will start it is impossible to say.

There are certain abnormal causes of corrosion and pitting sometimes met with which call for a word of remark. The pitting of iron propeller blades is not at all uncommon, and this almost always takes place on one side of the blade exclusively, and that the back. Mr. Weir* explains the action by the fact that as the propeller rotates there is naturally an increased pressure at the front side and a decreased pressure at the back. This decreased pressure leads to the evolution of oxygen from solution, and the liberated bubbles of oxygen coming in contact with the metal adhere and cause oxidation, ultimately leading to the formation of pits.

Iron and steel are never homogeneous. In malleable iron the mass is pure iron, but scattered through it are particles of carbide of iron, and also of intermixed slag and oxide. In mild steel, also, the mass is pure iron

* Trans. Institution of Engineers and Shipbuilders, Scotland. Vol. xl., page 79.

(ferrite), but scattered through it are particles of carbide of iron (in both cases in the form known as pearlite); whilst in grey cast iron the mass is an impure iron containing silicon and other elements, whilst scattered through it are flakes of graphite and small masses of carbide of iron and other compounds. It would seem, therefore, that just the conditions required to set up electrolytic action are present, for a small potential difference would be produced between carbide of iron and iron, and a very considerable difference between graphitic carbon and iron, to say nothing of the other impurities present in pig iron, and, therefore, electrolytic action has frequently been called in to account for the corrosion of iron and steel in sea water.

It is well known that when cast iron is exposed to the action of sea water for a long time it undergoes complete disintegration, the iron is dissolved away, and a soft, spongy mass of graphite, carbide of iron, and other substances is left. This, of course, is exactly what would be expected under the influence of electrolytic action, the electro-negative carbon being left, whilst the electro-positive iron is dissolved away; but it will be seen also that it is exactly what would happen under the influence of purely chemical action, since the iron is oxidised by air, carbon dioxide, and water, whilst the carbon is not, so that as far as this particular action is concerned one explanation will be as satisfactory as another. If the corrosion were due to electrolysis, it would be expected that the cast iron containing a large quantity of the spongy electro-negative carbon would be most readily

attacked, but this is certainly not the case. It is generally admitted that cast iron is less readily corroded than either wrought iron or mild steel. Experiments recently made showed in the laboratory very little difference between malleable iron, cast iron, and steel as regards their resistance to corrosion by sea water, but on such a matter laboratory experiments are not by any means conclusive.

It is, of course, impossible to say that electrolytic action does not take place, especially as electrolytic and chemical action are so closely related, but whilst such action might be expected, it has not been proved, and the phenomena of the corrosion of iron and steel in sea water do not necessitate the calling in of any such action.

There are, no doubt, many causes in operation that may promote or retard the action of sea water, and thus help or retard the destruction of iron structures. In estuaries and near the shore there may frequently be traces of acid and other matters which may greatly accelerate corrosion. These may be in solution or in the form of scum, which may settle on the metal. Also, it may happen that there may be differences in the composition of the water at different depths, and a metal immersed in two solutions which differ will as surely set up an electric current as two metals in the same solution. Such conditions may sometimes explain abnormal cases of corrosion.

Iron exposed to the sea becomes rapidly coated with living organisms of various kinds, but as far as can be

judged these do not accelerate corrosion, though from other points of view they are very objectionable.

Iron which is to be immersed in sea water must, wherever possible, be protected from the corrosive action by a suitable covering. The paints or compositions used are in general of two kinds—anti-corrosion compositions, which have for their object the protection of the surface from corrosion, and anti-fouling compositions, which have for their object also the prevention of the adhesion of living organisms.

Ordinary paints are of little use in protecting iron from the action of sea water, and most metal coverings are still less efficacious. Of the coating materials, the most satisfactory are the black asphalt varnish solutions, made mostly from coal tar products, which are now largely used. Bitumastic enamel or solution, which has been already mentioned, is found to be satisfactory. This has been used for floating buoys on the Clyde with considerable success; but no covering can be expected to resist the action of air and sea water for an indefinite period.

Anti-fouling compositions depend on the presence of some substance which will either prevent living organisms attaching themselves to it, or which will destroy them when they have become attached, the latter action being due to the presence of some poisonous material in the composition. Very many substances have been suggested, and Newman, after giving a long list of the substances that have been used, many of which are obviously quite

useless, states that the most efficient material yet suggested is the gum euphorbium. The gummy juice is mixed with the colouring matter and used in the ordinary way. Newman says:* "Euphorbium paint has undoubtedly many natural qualities, especially when applied to metallic surfaces, and the juice of euphorbium has a strong affinity for iron and steel. It is a reliable preservative against fouling, rust, and the corroding action of bilge water, it is easily applied without preparation, and has no injurious effect on iron, wood, or any substance generally used for engineering purposes. It prevents marine worms, barnacles, and vegetation adhering to a surface coated with it, until its protective qualities become exhausted with time; the bitter pungent juice of euphorbium paralysing all efforts of marine and insect life. It maintains its quality in all climates, and retains its virtues for a considerable time, and is most tenacious and yet elastic, for the prepared euphorbium can be drawn out to a thin rod. It does not blister, crack, or scale, and its viscosity is such that it will adhere to polished steel, tin, zinc, lead, or any smooth surface, and also to pipes buried in the earth. . . . It is the most important and novel substance naturally possessing the necessary poisonous principle recently introduced into the manufacture of anti-fouling and anti-corrosive compositions and paint for submerged or peculiarly exposed structures, and it is doubtful whether, for ships trading in any but very clean waters, and for submerged

* "Corrosion and Fouling of Metallic Structures," page 348.

structures generally, there is a better material to employ, or one its equal for protecting the bottoms of vessels or any metallic surfaces from fouling and corrosion."

The author makes this long quotation because of the importance of the subject, and because he has not yet had an opportunity of making experiments with euphorbium, nor is he aware of any published papers in which details have been given.

The question of the relative corrodibility of the various forms of iron is one of great interest, and it is also one on which there has been great divergence of opinion. The results of experiments made by different observers have also given very different results, and from the data at present available it is impossible to draw any absolutely certain conclusions.

There are many reasons for this. The first is that the condition in which the metal is used may vary—*i.e.*, whether it is cleaned or left with a more or less adherent layer of oxide; and the second is that the terms "iron" and "steel" are very vague, materials known by the same name not being by any means identical. Malleable iron has a nearly definite composition, but steel has not. Mild steel for most purposes is selected according to its physical properties, and the percentage of carbon which it contains, and other constituents which may be present in small quantity, whilst having little effect on the physical properties, may have considerable influence on corrosion.

The author will, therefore, state the conclusions to which he has come, without attempting to go into

details, or to give the evidence on which his conclusions are based, and it must be remembered that the conclusions are general, and may not be borne out in every particular case.

(1) That the corrodibility of the metals in the atmosphere, in fresh water, and in sea water follows generally the same order.

(2) That cast iron resists corrosion better than any other form of iron and steel, the close-grained irons being less acted on than the more open-grained varieties. He is at present unable to say which constituents have most influence on the durability. Cast iron, which is left with the skin as it comes from the mould, is less easily corroded than that which has been machined.

(3) That malleable iron is, as a rule, less easily corroded than mild steel, but experiments do not always show this to be the case. The purer the steel, the less it seems to be corroded, and probably very pure steel would have about the same rate of corrosion as malleable iron, and it would probably be safe to say that for most purposes there is little difference between the two metals. Where, however, resistance to corrosion is important, it is safer to use malleable iron. The evidence on this point is very conflicting, but the opinion of practical users is very strong that malleable iron resists corrosion better than mild steel. The foreign constituents present in steel seem to have a marked effect on its durability, but the author is not at present able to say which constituents promote and which retard corrosion.

There is another point of interest that may be mentioned, and that is the effect of strain on corrosion. Prof. Barr has pointed out that in boilers corrosion in the form of grooving takes place most rapidly on those parts which are subject to bending strain, the action being due to the fact that the scale is constantly broken off, and fresh surfaces are exposed to corrosion, and thus corrosion may be considerably accelerated. The mere fact of a metal being under stress may also modify the corrosive action.

CHAPTER VII.

CORROSION OF COPPER AND BRASS BY SEA WATER.

FEW metals are used in positions or under conditions where they are likely to be acted on by sea water, and alloys are usually used in such cases in preference to the pure metals. Copper is, however, sometimes used for water and steam pipes of various kinds on shipboard; lead is also used for pipes, and of late aluminium has been used for shipbuilding and other purposes.

COPPER.

In ordinary fresh water copper is very slightly acted on, no loss of weight being detectable after long immersion, and no green deposit being formed. The action of sea water on copper is, however, very rapid, a green deposit being formed in a very short time, and rapidly increasing in quantity. A small part adheres to the metal, but the greater portion is non-adherent, and, therefore, falls away. For this reason, if the water be in motion, but little green deposit may be seen, though the copper is being rapidly corroded. The surface of the metal also becomes dark red from the formation of a small quantity of adherent red oxide.

A sample of the green deposit formed by the action of sea water on copper was analysed and found to contain:—

Copper carbonate (CuCO_3).....	29.77
Copper chloride (CuCl_2).....	8.39
Copper oxide	59.38
Water	2.46
	<hr/>
	100.00

It is thus a mixture of basic carbonate and chloride, and it is evident that the salts in solution play an active part in the corrosion. The oxygen and carbon dioxide and the chlorine of the chlorides in solution seem to act together in bringing about the change, the chlorides being the essential agents, since if these be not present the others have little action. The action does not take place, or at any rate takes place only to a slight extent, in sea water which has been well boiled, so as to expel oxygen and carbon dioxide, but it is not prevented by neutralising the water with lime. It appears, therefore, as if the presence of oxygen in solution as well as of chlorides is necessary for corrosion.

The destructive action of sea water on copper is well known, from the rapid corrosion of copper pipes used on shipboard. As in all other cases of corrosion of metals, the action is very erratic; sometimes it may be uniform over the whole surface, but more usually it takes place in spots, leading to rapid pitting and perforation. It is quite impossible to say what is the determining cause of corrosion in any particular spot, or why in

some cases it is so much more rapid than in others. It is, of course, easy to say that it is due to the quality of the metal, but the author has never been able to trace any case of the corrosion of copper to the quality of the metal used. It is very doubtful, also, whether a very pure copper has any advantage over the ordinary more or less impure commercial coppers. It is, indeed, possible, though on this point the author cannot speak definitely, that some impurities may retard and other may accelerate the action. The action is retarded by contact with metals which are more electro-positive than copper, such as iron and zinc, little or no action taking place till these metals are dissolved. The protective action seems only to extend over a comparatively small area, parts some distance from the point of contact being rapidly attacked.

Copper is quite unsuited for use in any position where it will come in contact with sea water, and should, therefore, be avoided for pipes on shipboard wherever possible. Corrosion is certain to take place, and it is only a question of longer or shorter time, usually shorter, before failure must result. It is impossible to protect the metal from corrosion. Tinning may have some slight influence in increasing its life, but not very much, so that the only safe plan is to avoid the use of copper for marine fittings altogether.

ZINC.

Zinc is never used by itself under conditions where sea water can have access to it, except as a positive metal to prevent the corrosion of other metals, but for

reasons that will be seen later the action of sea water on it is of some importance. It is readily acted on by both fresh and salt water, but more rapidly in the latter, in the presence of oxygen and carbon-dioxide, a basic carbonate being precipitated. For this reason, galvanising is not much protection for articles that have to be immersed in sea water.

LEAD.

Of all the metals in ordinary use, lead seems to have the greatest power of resisting sea water. On long exposure it loses weight slightly, and a small amount of white deposit, probably basic carbonate, is formed on the surface, but the action soon ceases.

ALUMINIUM.

This metal is acted on by sea water, a flocculent white deposit of hydrate being formed. The action seems to be due to the presence of salt in solution, since fresh water has little action.

Other metals are rarely used under conditions in which they can be acted on by sea water, but certain alloys are largely used, it being found that in many cases alloys resist the action of corrosive agents better than the simple metals.

Two sets of alloys are in general use—the brasses, which consist essentially of copper and zinc, and the bronzes, which consist essentially of copper and tin, small quantities of other metals being often added for various reasons, or for no reason. The variations that

are possible in alloys are so great that only a few of the principal ones, which may be taken as types, can be considered, and as at present very little has been published on the question of the corrosion of alloys, what is here given must be considered in the light of being a preliminary sketch to be filled up later as experiments and observations are made, and thus as details are accumulated.

THE BRASSES.

The brasses used in marine work may vary in composition from about 90 per cent copper and 10 per cent zinc to about 50 per cent copper and 50 per cent zinc. The properties of these alloys, of course, vary very much, but from the standpoint of the action of corrosive agents they may be divided into two groups—those containing more than 67 per cent of copper and those containing less than that amount, these two groups being separated by well-marked characteristics.

The structure of alloys, as is now well known, varies very much, and the structure may be determined either by examination under the microscope or by noting the solidifying point, or points, by means of an accurate pyrometer. If an alloy containing, say, 70 per cent of copper and 30 per cent of zinc be melted and allowed to cool, it is found to have practically one solidifying point; that is, it solidifies as a whole at a definite temperature exactly as a pure metal would do. On the other hand, if an alloy of 50 per cent copper and 50 per cent zinc be examined, it is found to have two distinct solidi-

lying points; that is, first of all the larger proportion of the alloy solidifies, leaving a mass of still liquid material, and then as the temperature falls still further this also solidifies, so that such an alloy is a mixture of at least two constituents, which may vary in character.

The microscopic examination shows exactly the same thing. If a piece of 70/30 brass be properly etched and examined under the microscope, it is found to be a uniform mass of crystals. The crystals may be large or small, according to circumstances, but they are all alike, the alloy having crystallised exactly as if it were a single substance, whilst if the 50/50 alloy be examined it will be found to consist of at least two portions. There will be a mass of crystals, but these, instead of forming the whole of the mass, will be separated by a network of a different material, in which they are embedded, the ground mass having evidently solidified after the crystals had been formed. These differences, as we shall see, have a very marked effect on the resistance of the metal to corrosion.

It is not necessary to enter into any discussion of the nature of the substance which forms the crystals when a rich brass solidifies. It is not a pure metal, for it contains both copper and zinc. It is not a definite chemical compound, for the copper and zinc are not present in simple atomic proportions, and besides, these proportions may vary within wide limits; it is not a mere mixture of copper and zinc, for the properties of

the alloy are not by any means a mean of those of its constituents, and whatever it may be, it will be simplest to regard it as being a solid solution of zinc in copper; a solution, that is, which has solidified without the separation of its constituents, and therefore retaining in the solid condition the general characters of a solution.

When an alloy of copper and zinc, containing, say, 70 per cent copper, and which, therefore, has solidified as a whole, is immersed in sea water, it is acted on, though not so rapidly as copper, and both copper and zinc are dissolved out. This, indeed, is what would be expected from the action of sea water on the metals, which has been already discussed. The metals are not, however, attacked with equal rapidity, the zinc being removed more rapidly than the copper. If the alloy were a chemical compound it would either not be attacked or would be dissolved as a whole, but being only a solid solution, there is no reason why this should be the case, for many cases are known in which one liquid can remove a substance in solution from another, as, for instance, when ether is shaken up with an aqueous solution of bromine or iodine, the bromine or iodine is removed from the water and passes into solution in the ether.

The proportions in which the two metals are dissolved do not seem to be definite, but there is always a much larger proportion of zinc dissolved than copper, the ratio of copper to zinc dissolved varying from about 1:5 to 1:10. As in the original alloy the proportion of copper

to zinc is about 2·3:1, it will be seen how much more readily the zinc is dissolved than the copper. As a result, the alloy always undergoes what is called dezincification; that is, the zinc is dissolved away from the surface, leaving a layer of metallic copper. This action is well marked when brass rich in copper is pickled in dilute acid, the surface thus acquiring a red colour and being known as red brass. On long exposure to acid solutions the zinc may be so completely dissolved away that a distinct layer of copper, which may or may not be adherent to the unattacked brass, is left, or, in very extreme cases, the zinc may be almost entirely removed, leaving only a spongy mass of copper. Many such cases are known. The copper left will not, of course, represent the whole of the copper in the alloy, since some copper is always dissolved away by the solvent.

In the case of sea water, a small portion of the zinc may be removed in solution, but the larger portion and the copper which is dissolved forms a bluish deposit, which may adhere to the metal, but most of which will probably be non-adherent, and therefore fall away. Very frequently the zinc salts crystallise out on the surface of the metal in rounded nodules or in fine tufts of feathery crystals. The action will go on continuously, the metal being slowly dissolved away. It seems, however, to be more rapid at first when the metal is fresh, perhaps because the adherent deposit forms a somewhat protective film, but the action will not cease while the conditions are favourable for action.

The essential conditions are the presence of oxygen and carbon dioxide, for in well-boiled sea water there is very little action, only a trace of copper and very little zinc being dissolved.

The action seems to be a purely chemical one. At first sight it might seem that the conditions would be specially favourable to electrolytic action, but this is not so. The copper and zinc are in solution, one in the other, and therefore cannot set up a potential difference between them; and even after some of the zinc is dissolved away, so as to leave a mass of copper, electrolytic action will not be set up, it having been shown by Laurie that no potential difference is produced by the contact of copper with alloys containing such a large proportion of copper.

There is, of course, no doubt that electrolytic action may be set up if other substances are present, and the effect may thus be either to increase or diminish the action on the brass as a whole, or to increase or diminish the proportion of zinc to copper dissolved. If, for instance, the brass be placed in contact with substances that are electro-positive to it, and therefore to copper, the metal is almost completely protected. A fragment of iron or zinc will protect the brass from corrosion until the iron or zinc is completely dissolved away. It must be borne in mind, however, that the protective action extends only to a short distance from the point of contact, so that in the case of a large piece of brass it may be attacked at other places. This is on the assumption that the zinc or iron is merely resting against the brass; if it be suspended

opposite to it by means of a conducting wire, the protected area will be much greater.

In several cases where pieces of 70/30 brass were kept in sea water, which was frequently changed, for eight months in contact with iron, the brass did not lose in weight, and neither copper nor zinc passed into solution; and the result was the same whether malleable iron, steel, or cast iron was used.

On the other hand, when a substance electro-negative to copper, and therefore to the brass, was used, the result was always to greatly increase the corrosive action, at the same time the proportion of copper to zinc dissolved being, as a rule, much larger than when sea water alone was used.

For example, pieces of 70/30 brass were immersed for some months in sea water in contact with coke and graphite. In the case of the coke the ratio of copper to zinc dissolved was 1.2 to 1, and with graphite 1.6 to 1. In an experiment in which the sea water was heated to about 150 deg. Fah. the ratio of copper to zinc was with coke 1 : 1.13 and with graphite 1 : 1.35; and in each case the total loss of weight was greater than under the influence of sea water at the ordinary temperature.

With certain other substances somewhat curious results were obtained. If, for instance, the brass was moistened with ammonium sulphide, so as to form a black film, and then immersed in sea water, the action seemed to be considerably increased, as also was the proportion of zinc to copper removed.

It has frequently been stated that the destruction of brass by sea water may take place in three ways:—

- (1) Corrosion proper;
- (2) Dezincification;
- (3) Erosion.

By corrosion proper is understood cases in which the copper and zinc are removed together, so that the metal diminishes in weight, but otherwise remains unchanged; whilst by dezincification is understood those cases in which the zinc is dissolved away and copper is left; whilst by erosion is understood the mechanical wearing away of the metal by friction.

Corrosion as defined above never takes place, and corrosion is always in the first instance dezincification. Where it seems as if the two metals have been equally attacked this is due to the influence of erosion. The copper left when the zinc is dissolved is always more or less spongy, and is therefore easily worn away mechanically, thus giving an appearance as if the two metals had been equally attacked. If there be a rapid current of sea water over a piece of metal, especially if the water be loaded with solid matter which can assist erosion, the spongy copper may be rapidly worn away, so that the metal will lose greatly in weight and will decrease in thickness. On the other hand, if the water be still, or its motion sluggish, the spongy copper will not be removed, and the loss of weight will be only that due to the metals removed in solution; and this action may continue till the piece of brass may be completely dezincified, and, whilst retaining its form, may be

reduced to a mass of spongy copper. If the action is rapid, owing to the presence of very acid liquids, there may be a sharp line of demarcation between the unaltered brass and the dezincified layer, leading sometimes even to the complete separation of the latter; whilst if the action be slow, as under the normal action of sea water, the dezincification will extend gradually into the metal, there being no sharp line of demarcation between the two layers.

Local dezincification is very easily set up on ordinary brass in sea water, contact with a more electro-negative substance being usually sufficient to start the action. If, for instance, a piece of 70/30 brass be immersed in sea water in contact with a flake of graphite or a piece of coke, action will at once begin, and a marked dezincification will be observed beneath the graphite or coke. Many other substances have a similar action. Whilst iron, as already pointed out, is electro-positive to the brass, and therefore, to a certain extent at least, protects it, oxide of iron, or, rather, the hydrate produced by the corrosion of the iron, is electro-negative, and thus tends to destroy the metal. Copper scale, on the other hand, seems to have no action. Pig iron also exerts a protective action, but as it is oxidised the flakes of graphite which it contains may settle on the metal and exert a destructive action. In order, therefore, that brass may attain a maximum durability, it is essential that it should be carefully protected from all substances which are electro-negative to it, and which, therefore, would tend to promote corrosion.

The protection of brass from corrosion in sea water is a matter of great practical importance, but at present no satisfactory method of protection is known. It is doubtful whether the addition of any other metal in small quantity will retard corrosion. The Admiralty specify the addition of 1 per cent of tin to the brass to be used for condenser tubes, making the composition—copper 70, zinc 29, tin 1, per cent; but it is uncertain whether this is of any real advantage. Tubes are often tinned inside; but here again, whilst in some cases the tinning seems to have served a useful purpose, in others no advantage has been detected. The author believes that no alloy that can be used for condenser tubes is more durable than good 70/30 brass.

CORROSION OF CONDENSER TUBES.

The most important case in which the corrosion of brass has to be considered is that of the corrosion of the condenser tubes in sea-going steamships, and this is important not only from the frequency with which it occurs, but also for the extremely erratic way in which failures take place. It often happens that a set of tubes will fail after a comparatively short period of use, whilst another set made under exactly the same conditions may last a long time. The author has come across tubes that have lasted ten or more years, whilst in another case they failed after six weeks' use.

Corrosion may take place both from the outside, or steam-side, and inside, or water-side, but the serious

corrosion is almost invariably the latter. When a condenser tube fails it is usually from the formation of one or more irregular holes. These holes are funnel-shaped, the larger diameter being inside the tube, and the holes are almost always ranged in a line, which is at or near the lowest part of the tube when it is in position. Very frequently, in addition to the holes, there are what seem to be plugs of copper, extending from the inside of the tube, perhaps quite through. The copper is spongy, and when the "plug" goes right through it is easily pushed out, leaving a hole. These copper "plugs" are often overlooked, because when the tube is removed it is coated outside with a layer of grease, and the engineer is not interested in making a careful examination of the old tube. All he wants is to get the old tubes out and the new ones in as rapidly as possible.

It has been suggested that these "plugs" might be fragments of copper left unalloyed in the manufacture of the tube. This is, however, quite impossible, for the plugs are always roughly circular, whilst any fragments left in the alloy would be drawn out into a fine thread in the process of drawing through which the tube goes between the time it is cast and when it is finished.

When the tube is taken from the condenser, it very frequently contains a considerable amount of deposit. It may be almost free from deposit, the interior being rough and dark coloured from the presence of copper oxide, or it may contain a considerable quantity of deposit. This deposit may be greenish or black, in

which case it is probably made up mainly of material derived from the tube, and it may contain, scattered through it, masses of white needle-shaped crystals, or nodules of zinc salts, or it may be brown, in which case it always contains a considerable quantity of hydrate of iron. When tubes have corroded badly they are usually found to contain a considerable quantity of deposit.

A sample of deposit taken from a badly-corroded tube was found to contain—

Copper oxide	30.85
Copper chloride	3.20
Zinc oxide	30.80
Iron oxide	11.40
Insoluble matter	3.08
Carbon dioxide)	
Organic matter)	20.67
Water	
	<hr/>
	100.00

The oxide of iron and insoluble matter cannot have been obtained from the corrosion of the tube itself, but must have been brought in from outside.

The presence of a large quantity of deposit such as that above mentioned indicates (1) that foreign solid matter is being brought into the tube with the water; and (2) that the circulation was defective, or at anyrate that the current was not strong enough to keep the tube clear.

From what has been said above on the action of sea water on brass, it is quite evident that all condenser tubes must be corroded in time, and that the corrosion will

always in the first instance be dezincification, but whether the spongy copper left will remain in the tube or whether it will be removed will depend upon the eroding power of the water.

Tubes that have been in use for many years are always more or less uniformly worn away, the thickness often being reduced to an average of less than one half the original thickness before a hole is formed anywhere. On the other hand, when tubes are badly corroded or fail quickly, the action is much more irregular. The average thickness of the tube may be little reduced, the corrosion being concentrated on certain spots.

The formation of the holes in a condenser tube at once suggests local electro-chemical action. It is quite certain that it is not due to anything in the brass. Brass condenser tubes are of uniform composition, and even if they were not, slight variations in the percentage of copper in places would not set up electrolytic action. Nor are there any impurities present that could have this effect. A very large number of samples of condenser tubes, both those which have stood well and those which have failed quickly, have been examined, but in no case has any foreign matter been found. It has also been found that corrosion may take place just as rapidly when the tubes are made of the very purest metals obtainable as when the more impure—though still comparatively pure—metals of commerce are used. Owing to the severity of the mechanical process of drawing, only comparatively pure metals can be used.

It has been suggested that the corrosion may be set up by a largely crystalline condition of the metal, the differently oriented crystals setting up electro-chemical action. No evidence whatever has been produced to show that crystals of brass can set up such action one on another, and as in any case the largest crystals are microscopic, this would certainly not account for local corrosion. The size of the crystals in brass tubes does undoubtedly vary very much, but the author has examined a very large number of tubes, and has found that the good and the bad, as measured by the time they have lasted in actual work, are equally distributed between the coarsely and finely crystallised specimens, so that the size of the crystals, whatever influence it may have on the physical properties, has nothing to do with the power of resisting corrosion.

If the corrosion is not due to the metal, it must be due to something external to the tube, and the author is convinced that this is always the case, though he knows that this is not the opinion of many marine engineers. The blame being laid on the metals seems to be due to two causes: (1) That it is always easier to blame someone else; and (2) that the causes of the corrosion are so obscure that it is very difficult to trace them. Two steamers may be working under apparently similar conditions, yet in one the tubes last well and in the other they fail rapidly, and therefore it is natural to think that the metal is at fault. Against this may be put the similar fact that tubes of exactly the same composition and make may be supplied to two steamers; in

one they may stand well, and in the other they may fail rapidly.

As a matter of fact, there are so many possible differences in the conditions of working, depending on the character of the water used and the care which the engineer takes of his condenser, that one can never say for certain that the conditions under which the tubes have been placed in two steamers are the same.

The rapid and irregular corrosion of the tubes seems to be always due to the presence of some foreign substance which can set up electrolytic action, and thus lead to local corrosion.

It has been suggested that the cause may be fragments of copper scale left inside the tubes by the maker. This, however, is certainly not the case, for copper scale does not set up action on brass.

The most likely substance is carbon, which, in any form, rapidly starts corrosion. Cinders may easily be drawn in to the condenser. On such a river as the Clyde, cinders, charcoal, and other materials are very common, and may easily be drawn in with the feed water. In one case, indeed, a cinder was actually found embedded in a condenser tube. Very frequently ashes are discharged in such a way that they can be drawn into the condenser.

When the condenser doors are made of cast iron, these will rapidly corrode unless well protected with cement or otherwise. Any fragment of cast iron carried into the tube would protect it as long as any iron remains unoxidised; but, once oxidation is complete, any

graphite left, and to a less extent the hydrate formed, would set up corrosion.

The action of foul river water in producing corrosion is much over-estimated. Of course, if the water be strongly acid, as it may be in certain rare cases, corrosion might be rapid.

If soluble sulphides be present, a layer of sulphide might be formed, and this might lead to corrosion when the tubes were again filled with salt water. It has been found that tubes alternately filled with river (Clyde) water and sea water are much more rapidly corroded than by sea water alone.

A dirty river water may contain also oily matter floating on the surface, which, if drawn into the tubes, would adhere, and thus perhaps cause the retention of injurious solid matter which otherwise might be carried away.

It is, of course, impossible to protect condenser tubes by any internal coating, and the only method of minimising corrosion is to work the condenser under the best possible conditions.

The iron condenser door must be well protected, so that iron or graphite cannot find its way into the tubes. The circulation should be rapid, so as to keep the tubes clear of sediment. This is of the utmost importance, as if there is no sediment there will be no local corrosion.

The tubes should never be left full of water when out of use, but the condenser should always be drained dry, and if the water last used was foul, it should be

flushed out with clean water. The tubes should be frequently cleaned, to remove deposit.

If these conditions were always attended to, there would be fewer cases of mysterious corrosion.

Other agents may exert a considerable corroding action both on brass and copper, especially at high temperatures, the most important of these being fats and oils. These are decomposed under the influence of steam, as already remarked, and both copper and zinc are very readily attacked by the liberated fatty acids. To this is no doubt due the corrosion which sometimes makes its appearance on the steam side of condenser tubes.

POOR BRASS.

When a brass much poorer in copper than 70 per cent is exposed to the action of sea water, the conditions are very different. The brass now consists of two separate portions, the one much richer in copper than the other, and these two portions set up a potential difference which is about the same as that produced between copper and zinc, and, therefore, electrolytic action goes on freely; the poorer constituent being rapidly dissolved, whilst the richer is not attacked. The loss of weight is much greater than with 70/30 brass, and the ratio of copper to zinc removed is very much less. In one set of experiments the ratio of copper to zinc was 1—14 and 1—214. Sea water thus acts as a very efficient etching agent, removing the material poorer in copper, and therefore showing the structure of the alloy. With a 50/50 brass

the action of sea water is very rapid, but no copper is removed, the dissolved material being entirely zinc.

It will be seen, therefore, that poor brass is quite unsuitable for use in any position where it is to be subjected to the continuous action of sea water or any other corroding agent. As brazing metal, which is used for the brazing of copper and brass, is always a poor brass, it follows that brazed sheets or tubes are quite unfit for use under such conditions.

When a brazed tube is exposed to the action of sea water, the disintegration is usually very rapid. The metal itself is not attacked, but the brazing is rapidly destroyed, a spongy, brittle mass being left, owing to the removal of the zinc of the brazing brass, so that the tube can quite easily be broken at the join.

The corrosion of brass in the case of the richer brasses seems to be entirely a case of chemical action, except where electrolytic action is set up by the presence of foreign substances, whilst in the case of the poorer brasses the action is primarily electrolytic, and is much more rapid. It follows, therefore, that only rich brasses, say 70/30, should be used in positions where they are exposed to sea water, and that even these will decay in time.

CORROSION BY MINE AND OTHER ACID WATERS.

Where the water is distinctly acid, as may be the case where acid liquors are sent into a stream, or in the case of mine waters, the action will be one of dezincification, and may be very rapid. Water containing 1

per cent of sulphuric acid—which is probably more than could ever be present in mine water—has a very distinct action on brass, but the surface of the metal remains clean and bright, the dissolved zinc passing into solution, and local dezincification under electro-negative substances, such as coke or graphite, is very much more rapid than with sea water.

BRONZES.

The bronzes consist of copper alloyed with tin, usually in the proportion of about 90 per cent copper and 10 per cent tin, with or without the addition of small quantities of zinc. The bronzes are much less readily acted on by sea water and other corrosive agents than are the brasses or than copper; but when any considerable quantity of zinc is present, zinc and copper are dissolved very much in the same way as in the brasses.

Of other alloys, very few are used under conditions such that they are exposed to the action of corrosive liquids such as sea water, and, therefore, they do not call for consideration here. Manganese bronze is said to resist powerfully the action of mine and other acid waters.

LITERATURE OF CORROSION.

The literature of the subject is, unfortunately, very scanty. Of books dealing with corrosion, which,

however, only deal with iron and steel, two may be mentioned:—

- (1) “Metallic Structures: Corrosion and Fouling, and their Prevention.” John Newman. London: E. and F. Spon. 1896.
- (2) “Iron Corrosion: Anti-fouling and Anti-corrosive Paints.” L. E. Andés. London: Scott, Greenwood, and Co. 1900.

Of papers read before societies there are a few, some of which have been quoted. The most important of recent date is “The Decay of Metals,” by J. T. Milton and W. J. Larke (Proceedings of the Institution of Civil Engineers, Vol. CLIV.).

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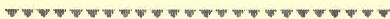
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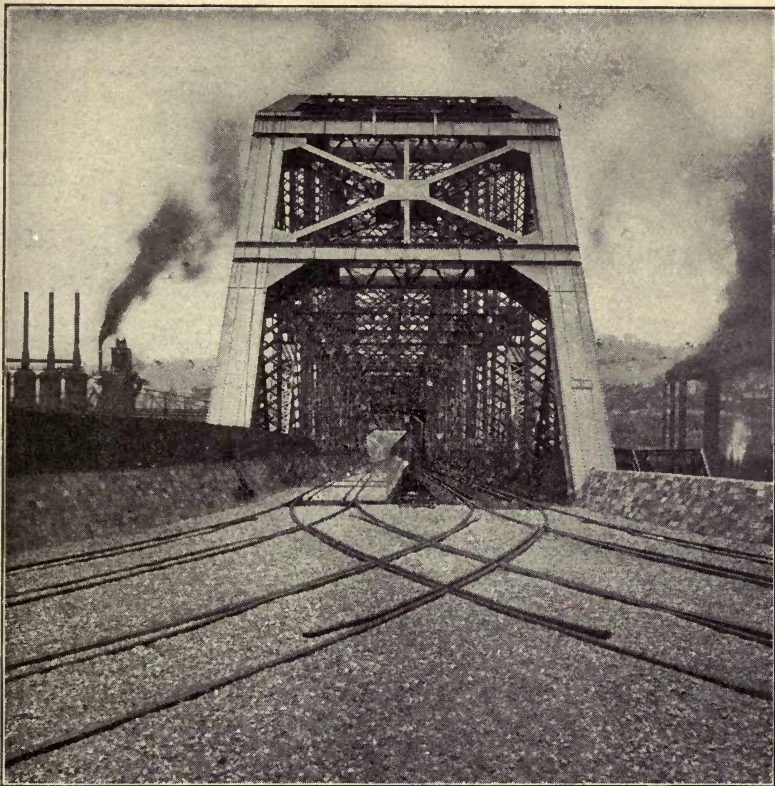
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